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Annual Report 1989 Chemistry Department

Edited by Jytte Funck, Aase Neve Larsen, Elfinn Larsen and Ole J. Nielsen

Risø National Laboratory, DK-4000 Roskilde, Denmark
March 1990

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ANNUAL REPORT 1989
CHEMISTRY DEPARTMENT

Edited by Jytte Funck, Aase Neve Larsen, Elfinn Larsen and Ole J. Nielsen

Abstract. This report contains a brief survey of the main activities in the Chemistry Department. The names and abstracts of all articles and reports published and lectures given in 1989 are presented. The facilities and equipment are mentioned briefly. The activities are divided into the following groups: radioisotope chemistry, analytical- and organic chemistry, environmental chemistry, polymer chemistry, chemical reactivity, mineral processing, and general.

March 1990
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This report contains a brief survey of the main activities in 1989 in the Chemistry Department including a listing of all articles and reports published and lectures given. The facilities and equipment are mentioned briefly.

The activities are divided into seven groups:

1. Radioisotope Chemistry
2. Analytical- and Organic Chemistry
3. Environmental Chemistry
4. Polymer Chemistry
5. Chemical Reactivity
6. Mineral Processing
7. General

INTRODUCTION

From its start in 1956 till now, the CHEMISTRY DEPARTMENT had grown to be the largest scientific group at Risø, embodying an impressive list of activities such as waste disposal, isotope production, analytical chemistry, polymer chemistry, chemical engineering, chemical reactivity, hot-atom chemistry, positronium chemistry etc., where sometimes during the years one activity has replaced another. In all cases, however, the work produced by the scientists and technicians has been of high quality, in scope shaped to local needs as well as the scientific demands of the international community. The wave of reorganisation has now struck the CHEMISTRY DEPARTMENT, which formally disappeared on March 16, 1990, when its members were transferred to the new task-oriented departments of NUCLEAR SAFETY, COMBUSTION CHEMISTRY, MATERIAL SCIENCES and ENVIRONMENTAL SCIENCES. In this operation the ISOTOPE SECTION has acquired a special status.

The present report is thus the final one from the CHEMISTRY DEPARTMENT, Risø.

MAIN ACTIVITIES

1. RADIOISOTOPE CHEMISTRY

Part of the work in radioisotope chemistry continues to be performed in collaboration with researchers in the medical, geological, and archaeological fields from universities and hospitals. Certification work for the EEC Community Bureau of Reference continues to be a major effort, and in addition more than 200 results for a number af elements contributed to the certification of two Canadian reference materials. Papers on activation analysis and other methods of trace analysis were presented at several international conferences.

A new radiochemical method for the determination of vanadium in biological materials by neutron activation analysis has been developed and tested on human blood serum. Lyophilized serum was irradiated and decomposed with nitric acid under pressure in 30 s in a microwave oven; after addition of ^{48}V-labelled vanadium carrier, ^{52}V with 3.2 min half-life was isolated by extraction with 8-hydroxychinoline. The experimental detection limit was less than 1 mg/m^3.

U.S.A. and United Kingdom patents have been granted on the counting of rapidly decaying radioactive indicators. These were based on a post-graduate study made in cooperation with the Technical University of Denmark (DTH).

Energy-dispersive X-ray fluorescence has been applied to the determination of Cr, Cu, As and Pb in soil samples in a cooperative project with Danish Technological Institute.

In collaboration with the Metallurgy Department, three ^{60}Co calibration sources with activities of 1.5 TBq, 43 GBq and 4.5 GBq have been supplied to the Danish army.

Industrial irradiation of silicon has increased slightly with practically full utilisation of all irradiation facilities. Construction of a new horizontal facility for silicon ingots up to 5" diameter is almost completed and will be installed in DR 3 in spring 1990. In its present form this facility will increase the capacity only slightly, but will improve the quality of the irradiation.

Since neutron transmutation doping of silicon started 15 years ago in 1974, we have irradiated more than 100 tons of silicon.

Scientific Staff: Kaj Heydorn, Kirsten Andresen, Else Damsgaard, Ulf Jacobsen, Inge Overby Jensen, Jesper Jørgensen.

Technical Staff: Steen Bidstrup,Lene Birch, Jørgen Hanefeld-Møller, Jørgen Erik Hansen, Jette Iversen, Bente Jacobsson, Jytte Jakobsen, Bo Lars Jensen, Margit Elbek Jensen, Marianne Elsborg Jensen, Ole Bauer Johansen, Svend-Erik Kerchhoff, Merete Larsen, Leif Laursen, Kirsten Madsen, Helle Ottosen, Charlotte Petersen, Frederikke Klarskov Petersen, Gitte Rasmussen, Søren Walbom Sørensen, Mette Thomsen, Mads Wille.

Consultant: Leif Højslet Christensen

Guest Student: Soo-Kyoung Rhee, Ehwa University, Seoul.

Guest Scientists: Dr. Lin Xilei and Zhang Xiuzhen
General Research Institute for Non-Ferrous Metals, Beijing, China

Dr. Nuri Gras Rebolledo, CEN La Reina, Santiago, Chile

Dr. Haji Wood Abdul Khalik, UTN Puspati, Selangor, Malaysia

2. ANALYTICAL- AND ORGANIC CHEMISTRY

The Plasma Quad instrument to ICP/MS elemental inorganic analysis has proved invaluable in several projects concerning trace elements in environment, food, health, minerals etc. It has worked out to be important in characterizing and determining the stoichiometric composition of superconductors. The project under the supervision of the Physical Department has extended from the basic work with Y, Ba, and Cu

to involve rare earth and other not too common elements bringing up otherwise quite difficult analytical problems easily solved by ICP/MS.

In 1989 the **Laboratory for Hydrocarbon Characterization** completed the EFP-85/86 project. This was the initial phase of the laboratory with the establishing of experimental equipment and analytical routines. A final report of these activities is being written. In 1989 the Energy Agency granted a new EFP-89 project for a three-year period to characterize reservoir fluids from the North Sea in cooperation with the Laboratory for Energetics, the Technical University of Denmark. This new project entitled "Measurement and simulation of PVT-properties of oils and gasses from Danish reservoirs" is budgetted at 1.4 million DK and it initiates the second phase of the laboratory: the practical implementation of hydrocarbon characterization. Experimental characterization data will be used directly together with PVT-data to characterize reservoir fluids completely and simulate PVT-properties.

Physical Organic Chemistry/ Gas-Phase Chemistry

Studies of ions isolated in gas-phase and organic high-temperature chemistry are two main research areas in the field of physical organic chemistry.

As a result of our continuing interest in species belonging to the CH_3NO_2/ $CH_3NO_2^{+\bullet}$ potential energy surfaces, the isolelectronic NH_2NO_2 system has been investigated. Most interesting, the $NH_2NO_2^{+\bullet}$ appear as a promising precursor for beam-experiments on NH_2NO, the key intermediate in the ammonia-based after treatment process for NO_x-control of flue gasses.

In addition, the isomerization of the parent nitroethylene radical cation was elucidated by ^2H labelling experiments.

The CS_3 species has long been a challenge to the sulphur chemists. As a result of a fruitful cooperation between the Chemistry Department and the Department of Organic Chemistry at the Technical University of Berlin, CS_3 can now be recognized as a viable molecule in the gas-phase. Collision experiments, using state-of-art tandem mass spectrometry, in combination with extensive ^{34}S labelling techniques provided the experimental evidence for two distinct isomers.

The pyrolytical studies have focussed on the possible thermally induced 1,3-methyl shift in dimethyl carbonate and the corresponding mono-, di- and trithio analogues. The studies did rely heavily on the application of ^{18}O and ^{34}S labelling in combination with dedicated gas chromatographic purification.

The study on solid state kinetics, financed by the Danish Department of Energy within the frame of the EFP 88 programme, has been continued:

Determination of activation parameters for hydrocarbon formation from kerogen.

The project was initiated in July 1988. The work has been concentrated on developing a kinetic model to describe the pyrolytic decomposition of kerogen, by estimating activation energies and the Arrhenius factor for the formation of volatiles. The experimental technique applied is based on pyrolysis - gas chromatography.

It appears reasonable to assume that reactions taking place in the solid state at pyrolysis temperatures do not follow "nice" kinetic laws with integral reaction orders. As a variety of products typically are generated by pyrolysis of e.g. synthetic as well as natural occurring polymers, coals, kerogens, it is suggested that the overall reaction leading to volatile products can be described by n'th order kinetics, n being fractional.

In the simple case, where all solid material is converted directly to volatiles, the solid state kinetics can be based on the following rate equation:

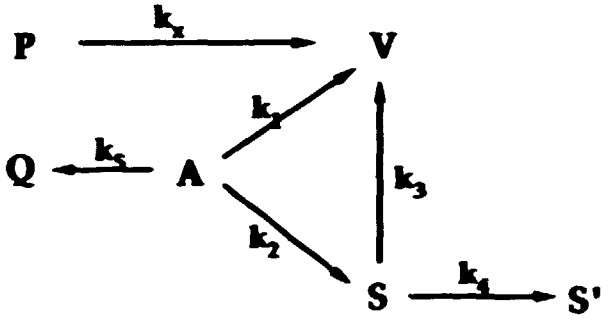
$$\frac{d(A)}{dt} = -k(A)^n$$

which gives rise to the following integral expression

$$(1 - \frac{C}{A_0})^{1-n} = (n-1)A_0^{n-1}kt + 1$$

where C is the amount of product formed and A_0 is the original total amount of pyrolyzable material.

However, if consecutive and parallel reactions are operating, e.g. producing a second solid phase, which is consecutively converted to volatiles, the system becomes rather complicated. The kinetic evaluation of such systems will be discussed based on the following model in which all reactions are considered to be of n'th order.



A denotes the starting material, whereas V and S are the volatile and solid products of the primary reaction. Reactions 3 and 4 of the solid S may consecutively lead to volatiles, V, and a solid product S', which is assumed to not be converted into volatiles. A non-volatile product Q, generated directly from A, which is not consecutively converted into volatiles is also taken into account. Finally, the parallel reaction of P into volatiles is considered, P being dissolved volatile material in the starting material A.

In the following the kinetic evaluation of the system will be discussed based on the assumption that all reactions are considered to be of n'th order, n_i not necessarily being an integer.

According to the above reaction scheme, the system can be described kinetically in the following way

$$\frac{dA}{dt} = -k_1A^{n_1} - k_2A^{n_2} - k_5A^{n_5}$$

$$\frac{dS}{dt} = +k_2A^{n_2} - k_3S^{n_3} - k_4S^{n_4}$$

$$\frac{dV}{dt} = +k_1A^{n_1} + k_3S^{n_3} + k_xP^{n_x}$$

$$\frac{dP}{dt} = -k_x P^{n_x}$$

$$\frac{dQ}{dt} = +k_5 A^{n_5}$$

$$\frac{dS'}{dt} = +k_4 S^{n_4}$$

It is important to note that the model given here describes overall reactions, i.e. no distinction is made between the various chemical components being evolved during the pyrolysis. Thus, all quantities are absolute or relative mass measures, i.e. relative to the mass of some component that does not change during the pyrolysis.

The set of coupled first order differential equations are solved numerically by a Runge-Kutta method, reaction rates (k_i), reaction orders (n_i) and initial values of A, P and S being specified as input parameters.

The pyrolyses were carried out as so-called sequential pyrolyses, i.e. the pyrolysis temperature and -time were chosen in a way such that each pyrolysis afforded only fractional decomposition of the sample. Typically 8-12 pyrolyses of the same sample were carried out at temperatures around 600K. The remaining pyrolyzable part of material was eventually volatilized by pyrolysis at very high temperatures, 1100-1200K.

The kinetic evaluation was carried out applying the computer code PYROLIB, which is based on a Runge-Kutta procedure for solving coupled first-order differential equations. The program is developed using the built-in facilities of the HP-5895A work-station and designed to read the report-files, giving the integrated GC-results directly. The program calculates and plots the time-dependent amounts of each of the six components involved together with the experimental values of V, obtained from the gas chromatographic analysis of the volatiles produced during the pyrolysis. As a guide for the otherwise manual fitting of the calculated data to the experimental data, the program finally calculates the sum of the squared differences between the experimental data points and the calculated amounts of volatiles at the same time. In addition, it finds the mean-, minimum- and maximum deviations between experimental and calculated values, the latter two being expressed as percentages of the experimentally obtained value.

The amount of combined pyrolyzate, V, is taken as the accumulated integrated peak-integrals, the total amount of pyrolyzable material being the final accumulated integral value obtained following the eventual volatilization of any remaining pyrolyzable material. Thus, the sum of the initial values of A, S and P equals the final accumulated integral value of V found during the pyrolysis.

The present work concentrates on evaluating the proposed model, using coal and kerogen samples with activation parameters known from other studies as model substances. For this purpose, a collaboration with the institute CREGU in Nancy has been initiated.

The original simple model has been described in detail in
L. Carlsen, A. Feldthus and P. Bo, J.Anal.Appl.Pyrol. **15** (1989) 373

In 1989 the **Mineral Analysis Group** completed work on an EFP-86 project determining geochemical criteria for reservoir quality. At the end of the year a report was published describing the results of the project (Risø-M-2779).

Work was continued with the energy research project "Temperatur-tidsvariationer i sedimenter fra det Danske Subbassin belyst via fissionssporstudier af udvalgte borekerner" within the framework of EFP-88 program. The project is a cooperative effort involving also the Risø Energy Technology Department and the University of Copenhagen (Institute of Petrology) and the Geological Survey of Denmark. Most of the analytical work (mineral separation, fission track counting) for three wells from the Danish Central Graben area was carried out during 1989. A simple model for calculating temperature-time history from fission track frequency distributions was developed. Most of the results of the study will be presented at several international meetings in 1990.

The research group continued work on the marine environment in cooperation with Hamburg and Kiel universities, which also included geochemical studies on marine minerals. At the 28th International Geological Congres in Washington D.C., the Mineral Analysis Group co-chaired and participated in a poster session on "Geochemical mapping on the ocean floor".

Applied geochemistry work, mainly on the evaluation rare earth elements in Irish granites were continued with Galway University College (Ireland).

Scientific Staff: Lars Carlsen, Asger Baltzer Hansen, Helmar Kunzendorf,

Elfinn Larsen, Per Solgaard.

Technical Staff: Helge Egsgaard, Jytte Funch, Per Ingemann Jensen, Ole Jørgensen, Lis Vinther Kristensen, Birgit Petersen, Susanne Petersen, Poul Sørensen, Niels Vinther, Hanne Voss, Jonna I. Carstensen.

Guest Student: Gilbert Ronald, Frankfurt University.

Guest Scientitists: Susanne Ebel, University of Hamburg.

3. ENVIRONMENTAL CHEMISTRY

The aim of the Environmental Chemistry group is to study processes in the atmospheric and terrestrial environment. Both experimental and theoretical activities take place.

In connection with the international evaluation of Danish environmental research in January, the section was visited by the air and the soil panel. Both were most positive in their estimation.

A thorough study of the different air pollution sources of polycyclic aromatic hydrocarbons (PAH) in two neighbourhoods of the international airport of Copenhagen has been performed. The final report will be available in April 1990.

The activities with the frame of the EEC nuclear research programme have been continued. The studies comprised "Geochemical modelling", "Geochemical databases", "Artificial materials", "The role of organics in the migration of radionuclides in the geosphere " and "Humic acid characterization". The three first projects are continuing in 1990.

For the Greenland Environmental Survey the Environmental Chemistry Section has monitored airborne dispersion of particulates in connection with exploration activities during the summer at the Nb mineralisation in the Sarfartoq area in West Greenland.

A study on enzymatically controlled iodination of naturally occurring organics as humic acids has been concluded in the frame of a Ph.D. study. The final report will be available by the end of January 1990.

The section has been the major force in the planning and organizing of three new interdisciplinary projects starting up in 1990:

1) TOR (Tropospheric ozone research). The Danish contribution to the European joint TOR programme within EUROTRAC consists of the three subprojects:

a) Composition and mass balance of NO_y
and the relation to O_3 and oxidized hydrocarbons,

b) Photochemical air pollution, and

c) Input from the stratosphere.

2) RIMI (Risø's integrated environmental project). The project aims at the study of pathways, processes and effects of anthropogenically derived nitrogen compounds in the environment.

3) MODECS (molecular design of chemical systems). The purpose of this interdisciplinary project is to cooperate on and support R&D activities concerning supramolecular chemistry, modifications of polymers etc. MODECS has 21 members and the initiative has been met with interest by industry and university laboratories.

Scientific staff: Peter Bo, Knud Brodersen, Lars Carlsen, Bror Skytte Jensen, Torben Nielsen, Karen Nilsson, Kim Pilegaard, Jesper Valentin Christensen.

Technical staff: Anders Feldthus, Hanne Jensen, Gitte Larsen, Anne B. Nielsen, Ingrid Pedersen, Jesper B. Rasmussen and Arne Vinther.

4. POLYMER CHEMISTRY

The low-angle laser light scattering (LALLS) detector has continually been used in characterizing water soluble polymers of different origin. The LALLS equipment is still the only one existing in Denmark for this purpose.

Experimental work on radiation grafting to polyethylene has resulted in a new matrix suitable for solid phase peptide synthesis and bioassays. Grafting has also been used to change the surface properties of hydrogels.

The mechanical spectrophotometers RMS 800 and RFS 8500 have been used in studies of both synthetic and biological polymers. The main projects have involved studies of dilute and semi-dilute solutions of

polystyrenes, and the gelforming pectin and actin systems.

The work on comb-shaped polyesters has progressed in several respects. In the first place a closer look is taken at the crystallinity of the aliphatic comb-shaped polyesters by use of infrared spectroscopy, X-ray diffraction, and differential scanning calorimetry (DSC) - a detailed understanding is still lacking. The second line is an extension of the number of available polyesters with the introduction of both aromatic dicarboxylic acids and a diol with two equally long side-chains. Finally, with the aim of studying polyester main-chain dynamics by FTIR, SANS and solid state ^{13}C NMR a new synthetic route to introduce specific deuteration in the methylene chain of long aliphatic dicarboxylic acids has been undertaken.

The Polymer Group has furthermore been involved in a project with characterization of wax precipitation in stabilized mineral oils. The amount of wax as function of temperature is determined by a pulsed NMR technique, and thermal effects are studied by DSC from -150 to +70°C.

A advanced Fourier-transform infrared (FTIR) spectrometer operational in a very broad spectral range from far to near IR, 30 - 10000 cm^{-1}, has been installed. The instrument is optically interfaced to an IR-microscope and has many modern accessories such as facilities for Photo Acoustic Spectroscopy (PAS), Diffuse Reflectance Infrared Fourier-Transform Spectroscopy (DRIFTS), and Attenuated Total Reflectance (ATR). The preliminary results obtained with PAS are promising especially since otherwise intractable samples can be investigated.

In collaboration with the Danish Society for Polymer Technology the entire Group was engaged in the preparation and organization of the 26th Nordiske Polymerdage, May 31 - June 2, at H.C. Ørsted Institute, University of Copenhagen, with 260 participants.

The Group also initiated the application procedure for a project entitled: "Polymersystemer med kontrolleret struktur og egenskaber" under "Det materialeteknologiske Udviklingsprogram" in collaboration with Institute for Chemical Technique, Technical University of Denmark, Coloplast A/S, and NKT A/S. The project is granted for a three-year period starting January 1, 1990, and is jointly supported by several Danish Research Councils.

Scientific Staff: Kristoffer Almdal, Kurt Heller, Søren Hvidt, Søren Hvilsted, Ole Kramer, and Walther Batsberg Pedersen.

Technical Staff: Lotte Hansen, Lene Hubert, and Anne B. Nielsen.

Guest Scientists: Prof. Wyn Brown, University of Uppsala, Sweden.
Prof. Paul A. Janmey, Harvard Medical School, U.S.A.
Dr. M. Mateev, University of Plovdiv, Bulgaria
Prof. R.F.T. Stepto, UMIST, Manchester, U.K.
Prof. V.T. Stannett, North Carolina State Univ., U.S.A.

5. CHEMICAL REACTIVITY

The main research activities in the section are chemical kinetics and spectroscopy. UV, IR and resonance Raman spectra of free radicals and molecules in excited states provide structural information on the short-lived reactive species, and they can be utilized in studies of chemical kinetics of elementary reactions. The section has one other research activity: Radiation Processing and Dosimetry.

Gas phase group

The pulse radiolysis technique combined with time-resolved UV and IR spectroscopy is employed in kinetic studies of free radicals occurring as intermediaries in atmospheric transformations and combustion.

We have continued our studies of oxygenated hydrocarbon radicals. The ultraviolet spectra of CH_2OH and CD_2OD have been recorded and O_2, NO and NO_2 were studied by monitoring the time profiles of the ultraviolet absorption signals of the radicals in the presence of varying amounts of the additives.

Peroxy radicals play an important role in the oxidation of hydrocarbons. In particular, isomerization of peroxy radicals into hydroperoxy derivatives, RO_2 -> QOOH, are thought to be a key step in the mechanism of autoignition of fuels. Ultraviolet spectra of a large number of peroxy radicals have been reported but so far virtually nothing is known about spectra and kinetics of the QOOH species. We have employed a simple source reaction, F + H-QOOH -> HF + QOOH and we have recorded the UV-spectrum of QOOH where Q= $(CH_2)C(CH_3)_2$, i.e. using t-butyl hydroperoxid as the parent compound. Our preliminary studies have been carried out at room temperature where the radical is relatively stable towards thermal dissociation. We want to employ the same fast source

reaction in future high-temperature kinetic studies of the dissociation reaction, QOOH -> epoxide + OH, which should give rise to fast chain reactions.

The experimental work on CH_2OH, CD_2OD and QOOH was carried out in collaboration with Christopher Anastasi, University of York.

Acetone is an intermediate in the atmospheric oxidation of various hydrocarbons and several laboratories are engaged in studies of the reaction mechanisms. The atmospheric lifetime of acetone is controlled by the reaction

$$OH + CH_3\text{-}CO\text{-}CH_3 \rightarrow H_2O + CH_3\text{-}CO\text{-}CH_2.$$

We have recorded the ultraviolet spectrum of the acetonyl radical, CH_3COCH_2, and studied the kinetics of the radical in the presence of oxygen. In the absence of oxygen the radical decays by simple second-order kinetics, but in the presence of oxygen we have observed transient absorption signals due to peroxy radicals produced in the reaction

$$CH_3\text{-}CO\text{-}CH_2 + O_2 \rightarrow CH_3\text{-}CO\text{-}CH_2\text{-}O_2.$$

The fate of the peroxy radical under atmospheric conditions is not known at present, but we intend to continue our investigations in order to establish a complete reaction mechanism for the oxidation of acetone.

The investigation of acetonyl and acetonyl peroxy radicals were carried out in collaboration with R.A. Cox, Harwell.

In the second year of a four-year EEC-funded (COST 611) collaboration with University College Dublin, investigations of the reactions of Cl and OH with organic nitrates have been completed. The temperature and pressure dependence of the reaction of OH with nitromethane have been studied. The international collaborations with Dr. Tim Wallington (Ford Motor Co.), Dr. Michael Kurylo (NASA) and Dr. Richard P. Wayne (Oxford University) were continued.

Water phase group

The study of the thermal decomposition of aqueous O_3 was continued. The results on the dependency of the temperature, pH and O_2 concentration, together with isotopic exchange ratios indicate a mechanism in which an electronically excited O_3 molecule originating

from the oxone dissociation-recombination reaction is the precursor for the free-radical-induced chain decomposition. An investigation of the H_2O_2-O_3 system indicates also a heterogenous initiation of the thermal decomposition reaction. The formation and destruction of H_2O_2 in acidic O_3 solutions depend to a great extent on the type of surface. It is likely that the chain decomposition of O_3 in acidic solutions is initiated by surface reactions.

Acetic acid has been used as an OH-scavenger in an attempt to obtain more information on the initiation reaction by quenching the chain decomposition. From these experiments the rate constant for the reaction of undissociated H_2O_2 with O_3 was obtained.

The work on high-temperature and high-pressure aqueous radical chemistry was focussed on determination of the activation energies of the reaction OH + OH and e^-_{aq} + OH. Some work was performed on radical scavengers effects at high temperatures in systems containing O_2, N_2O and H_2.

Investigations were continued on the mechanism of intramolecular electron transfer in model peptides. Kinetic and activation parameters for the electron transfer in Tyr-$(Pro)_n$-Trp and Tyr-$(Pro)_n$-Met series were measured. Formation of three-electron bonds: S∴S, S∴N and S∴O resulting from the electron transfer from methionine-containing model peptides was studied.

Physical organic chemistry (Raman group)

The work was concentrated on three areas: 1) The study of molecular dynamics of photoisomerization in excited electronic triplet states in solution. 2) Gas-phase studies of molecular dynamics in excited singlet states of 1,3,5-hexatrienes. 3) Studies of the photophysics of supramolecular compounds (crown-ethers) in solution.

In connection with the first topic, the collaboration with lic. scient. F.W. Langkilde (Pharmaceutical University), Prof. G. Orlandi and F. Negri (Bologna, Italy) and Dr. A.M. Brouwer (Amsterdam, The Netherlands) was continued. Molecular systems studied experimentally and theoretically were model compounds of general interest such as stilbene and 1,3,5-hexatriene. A Ph.D. study (B. Amstrup in colaboration with Prof. J.P. Dahl, Chemical Laboratory B, Technical University of Denmark) was finished sucessfully. The third topic was pursued in a joint project between Chemical Laboratory II; University of Copenhagen (Prof. K.

Bechgaard and A.M. Byrnard) and Radiometer A/S (lic. scient. N.-H. Jensen).

Finished Ph.D. projects: Bjarne Amstrup, "An ultraviolet resonance Raman intensity analysis of trans, cis, trans-1,3,5-hexatriene"

Radiation processing and dosimetry

Consulting work in connection with radiation processing is still growing concurrent with the growing use of radiation, mainly for sterilization of medical utensils and plastic modification. The consulting has concerned the establishing of new radiation facilities (in Sweden and in Belgium), characterization and calibration of existing facilities in Denmark and Sweden, and product validation for customers, also mainly in Denmark and Sweden. These dose measurements are also essential for the radiation processing which is carried out at the section's radiation facilities.

Our expertise in radiation processing and dosimetry has been utilized by various institutions in Denmark and abroad (Danish Board of Technology, Danish Industrial Council, American Society for Testing and Materials, CERN, IAEA).

A major conference on radiation processing was organized in The Netherlands in April 1989 (7th International Meeting on Radiation Processing). As programme chairman Arne Miller was responsible for the scientific and technical programme and co-editor of the proceedings to be published in 1990.

We have taken part in a successful development of balloon catheters with the Polymer Group and a Danish firm. This product is now produced by the firm with the use of radiation at the 10-MeV electron accelerator.

The collaboration with the National Physical Laboratory, UK (under the Euromet Programme) and the National Institute of Science and Technology, USA, has been important for establishing traceable dose measurements. Traceability is a key element for certified measurements according to international standards, such as the CEN 29000 series (ISO 9000), and steps have been taken towards accreditation by the Danish Institute for Fundamental Metrology as a reference laboratory for high dose measurements.

The Dosimeters used for the reference measurements are potassium dichromate, radiochromic dye films and calorimeters. Recently, an ESR spectrometer was acquired with the aim of using also the alanine dosimeter system in high-dose measurements. The spectrometer is not as

sensitive as the more expensive modern spectrometers, but it may be developed into a useful tool in quality assurance for radiation processing.

Scientific Staff: B. Amstrup, E. Bjergbakke, T. Ellerman, J. Fenger, J.W. Hansen, K.B. Hansen, J. Holcman, B. Lynggaard, A. Miller, S. Møller, O.J. Nielsen, P. Pagsberg, K. Sehested, A. Sillesen, R. Wilbrandt.

Technical Staff: H. Corfitzen, P. Genske, C. Hansen, E. Haugaard, T. Johansen, B. Kristiansen, E.E. Larsen, F. Larsen, M.B. Madsen, R. Madsen, J. Munk, M. Wille, A. S. Andersen, Sv. Nielsen.

Guest Scientists:

M.Mc. Michael Donlon, Dublin Institute of Technology, Ireland.
Dr. Howard Sidebottom, University College Dublin, Ireland.
Prof. Emil Ratajczak, University of Wroclaw, Poland.
Dr. Christopher Anastasi, University of York, England.
Dr. Fabrizia Negri, Dipartimento di Chimica, Bologna, Italy.
Dr. E.J. Hart, Port Angeles, USA.
Dr. Krzysztof Brobowski, Polish Academy of Sciences, Warsaw, Poland
Prof. Nikola Getoff, University of Vienna, Austria.
Dr. Sonja Solar, University of Vienna, Austria.
Prof. Joseph Rabani, Hebrew University, Jerusalem, Israel.
Dr. Andras Kovacs, Institute of Radioisotopes, Budapest, Hungary.
Dr. Hilbert Christensen, Studsvik Energiteknik AB, Nyköbing,Sweden.
M.Sc.Ulrik Kläning, University of Århus, Denmark.
Ms. Siriratana Biramontri, Office of Atomic Energy for Peace, Bangkok,Thailand.
Dr. William L. McLaughlin, National Institute of Standards and Technology, Gaithersburg, USA.
Prof. Anders Lund, University of Linköbing, Sweden.
Dr. Woon H. Chung, Pusan National University, Korea.
Marcelo Uzcategui, Nuclear Science Institute, Quito, Ecuador.
Dr. William L. McLaughlin, National Institute of Standards and Technology, Gaithersburg, MD, USA.
Dr. Bernhard Hickel, Sacley, Gif-sur-Yvette, France.
Dr. Igor Janovsky, Nuclear Research Institute, Rez, Czechoslovakia.
Dr. P. Lorenzetto, NET, Max-Planck Institut für Plasmaphysik, Garching bei München, W. Germany.
Dr. R.A. Cox, Harwell, UK.
Dr. Richard P. Wayne, Oxford University, UK
Dr. Michal Kurylo, NASA Headquarters, Washington DC, USA.
M.Mc. Ruaidhri Neavyn, University College Dublin.

6. MINERAL PROCESSING

The group has been working mainly with second phase of the implementation of the wet oxidation process on a semi-industrial scale. After studying the reactions in a bench autoclave, we have adapted the pilot plant pipe reactor to accept suspensions of clayey soil. The sample, which was provided by NKT Ltd., came from a former tar distillation site and was heavily contaminated by naphtalene, phenantrene, and other polycyclic compounds and from a site contaminated by DEHP. The chemical purification was very promising. Problems with material handling and filtration turned up, but were solved in some ways.

Zirconia recovery from eudialyte has been reviewed in anticipation of the inouguration of the Center for Advanced Ceramics. Corrosion of ceramics has been investigated.

Finally, the work on soil recovery has prompted an investigation of intermediates and expected end products from the wet oxidation of toxic compounds.

Scientific Staff: Jørgen Jensen, Emil Sørensen, Torkild Lundgaard, and Anne Belinda Bjerre.

Technical Staff: Helle Krogh, Jette Fosskov, Sv.Kr. Olsen, and Tomas Fernqvist.

Guest Scientist: Jia-Jun Ke, Beijing

7. GENERAL

The Department accomplishes chemical analyses and services for other departments at Risø, and on a commercial basis for external customers.

The Isotope Laboratory has continued to fulfil its commitment as the sole producer of neutron-irradiated materials for technical and scientific purposes in Denmark. The National Health Service has endorsed the plan

for organization and responsibility in the production of radiopharmaceuticals for medical diagnostics, and in collaboration with the Isotope Pharmacy a new radiopharmaceutical Cupri (^{64}Cu)chloride oral solution has been developed. According to EEC directives, all radiopharmaceuticals should be registered by January 1, 1992, and the registration procedure for one of our radiopharmaceuticals has been initiated. Radioisotope production mainly for scientific research has continued, and ^{60}Co sources for liquid-level measurements in cylinders containing liquified gas are produced.

As a supplement to the α, β and γ demonstration sources for educational purposes, ^{226}Ra sources for continuous cloud chambers are available. In addition to the regular supply to the Nordic countries 70 sets of demonstration sources have been supplied to Austrian schools through a Danish company.

The handling and disposal of radioactive wastes from Risø and other users of radioactive isotopes are taken care of at the Waste Treatment Plant.

A technical staff takes care of purchase, stocks, administration, typing, workshop, laundry, radioactive cleaning, etc.: Aase Neve Larsen, Kirsten Bay, Jytte Green, Ellen M. Jensen, Ester Andersen, Inger Jakobsen, Fini Lindskou, Svend Nielsen, Knud Larsen, Erling Christensen, Bent Villumsen, O. Sølling Hansen, Bent Nielsen, Jørgen Larsen, Svend Jensen, Signe Hansen, Birthe I. Hansen, Birthe N. Andersen, Pedro Breschiani, Ruth Ågensen, Palle Olsson, Winnie Andersen, Nina Thomsen.

Risø's Chemistry Department includes five geographically separated sections: the Chemical Laboratory, the Accelerator Department, the Radioisotope Laboratory, the Waste Treatment Plant, and the Mineral Processing Plant.

The staff of the department consists of 36 members with academic degrees, 3 Ph.D. students, and 67 technicians, including office personnel.

Fig. 7.1 The "doctor ring" of Chemistry Department is given to Lars Carlsen.

PUBLICATIONS

ATOMERNE STEDFÆSTER GAMMEL KERAMIK

Ingolf Thuesen and Kaj Heydorn

Ingeniøren, særtryk fra nr. 18 (1989)

Ved hjælp af neutron-aktiveringsanalyse lykkedes det forskerne at bestemme oprindelsen af en særlig form for keramik, fundet i en sumerisk oldtidsby.

Den sjældne keramik af typen »scarlet ware« viste sig at være lokalt fremstillet. Den indgik ikke i sumerernes omfattende handel.

EVALUATION OF ELEMENTAL CONCENTRATIONS IN HUMAN TISSUES AND BODY FLUIDS

K. Heydorn

Papers presented at the Second International Conference
on Elements in Health and Disease held in Karachi, Pakistan,
6th - 10th February, (1987) 347 - 359
Ed. by. Mohammed Said, M. Ataur Rahman and Lily Anne D'Silva

The vast amount of information available in the scientific literature on elements in human tissues and body fluids is not directly applicable for the purpose of distinguishing between health and disease. In fact it is often possible to find reported values for trace element concentrations in healthy individuals that differ so much that it is impossible to decide whether a particular result indicates excessive or deficient levels. Even good agreement with the mean value may only indicate that the same mistakes are repeated in many laboratories.

Independent reviews of the literature are therefore greatly needed to extract the best possible information from available data, but such reviews are difficult to prepare and therefore often not up to date. Methods for judging are not strictly objective, nor are they infallible; but a systematic approach combined with statistical tests has been found useful for testing the reliability of our own results, as well as those found in the literature.

FAST β- AND γ- RAY SPECTROMETRY

Henrik Kalfod Nielsen

Ph. D. project, September 1989

MANGANESE

Kaj Heydorn

In: Quantitative Trace Analysis of Boilogical Materials. Principles and Methods for Determination of Trace Elements and Trace Amounts of some Macro Elements.
Elsevier, Amsterdam, (1988) 471 - 485
Ed.by. H.A. McKenzie and L. E. Smythe

ACTIVATION ANALYSIS IN FOOD ANALYSIS VII. DETERMINATION OF VANADIUM CONTENT BY INAA METHOD IN VEGETABLE SAMPLES

S.A. Szabó, K. Heydorn and E. Damsgaard

Elelmiszervizsgalati Kozl. 35 (1989) 25 - 29

The base of determination of vanadium is vanadium - 51 (n, γ) vanadium-52 nuclear reaction. The half - period of vanadium - 52 is 3.76 minutes, typical γ - energy is : 1.4342 MeV. The samples were activated in 2.5 x 10 ^{13} n x cm $^{-2}$ s^{-1} thermal neutron by 10 sec, and were measured by Ge/Li detector with 1.61 keV energy - decomposition. The quantity determination limit is 10 ng.

FIRST-TRIMESTER DIAGNOSIS OF MENKES DISEASE: INTERMEDIATE COPPER VALUES IN CHORIONIC VILLI FROM THREE AFFECTED MALE FETUSES

T. Tønnesen, A.-M. Gerdes, E. Damsgaard, P. Miny, W. Holzgreve, F. Søndergaard and N. Horn.

Prenatal Diagnosis, 9 (1989) 159 - 165

Chorionic villus samples with copper contents of 1·91, 4·2, 5·6, and 6·3 ng/mg were observed in four cases with male karyotypes. These values were outside the range for unaffected males (0·30–0·85 ng/mg), and three of them were outside the control range (0·20–2·39 ng/mg). But these three values were below the values previously observed for affected Menkes fetuses (12·0–24·8 ng/mg).

Follow-up by ^{64}Cu uptake studies on the amniotic fluid cells was performed in three of these cases. A combination of ^{64}Cu uptake and chase experiments on the amniotic fluid cells showed more convincingly than ^{64}Cu uptake per se the direct copper values of 4·2 and 5·6 ng/mg to correspond to affected fetuses. Amniotic fluid cells from the male fetus with the CV copper value of 1·9 ng/mg showed normal results. The CV copper value of 6·3 ng/mg was considered pathognomonic for Menkes disease. The pregnancy was terminated, and the diagnosis was confirmed on fetal fibroblasts.

Maternal deciduum prepared from the placentae showed in one of the cases with an affected fetus copper values ranging from 1·5 to 5·7 ng/mg. In six additional diagnostic cases, the copper content was determined in both CV samples and maternal deciduum. In three of these cases with normal CV sample copper, maternal decidua values of 4·85–7·8 ng/mg copper were observed. These results show that maternal deciduum contamination of a CV sample could cause a false-positive diagnosis.

INSTRUMENTAL NEUTRON ACTIVATION ANALYSIS-APPLICATION AND LIMITATION

K. Heydorn

Fresenius' Zeitschrift für Analytische Chemie 334 (1989) 606 - 607

MINOR AND TRACE ELEMENTS IN MANGANESE NODULES AND SEDIMENTS FROM THE PACIFIC

H. Kunzendorf, R. Gwozdz, G. Friedrich and G. P. Glasby

In: THE PRACTICAL APPLICATIONS OF TRACE ELEMENTS AND ISOTOPES TO ENVIRONMENTAL BIOGEOCHEMISTRY AND MINERAL RESOURCES EVALUATION
(1987) 181 - 197

Ed. by R. W. Hurst, T. E. Davis and S. S. Augustithis

Sixty manganese nodules from five different areas of the Pacific Ocean, and 17 associated sediments were analyzed for 22 elements by instrumental neutron activation analysis. In particular, trace elements were determined.

Multivariate statistics of the data suggests that two to three element clusters represent the chemistry of the nodules. While one cluster is connected with Fe and includes elements As, La, Ce, Th, Co, Hf and Sc, the other composes Na, Sb, Zn, Ba, W and Br. Factor analysis reveals that the nodules from the five Pacific areas are geochemically different. Too few data were available to make statistically sound conclusions for the sediments.

North-American shale normalized rare earth element patterns of nodules and sediments are generally similar. However, while sediments always have Ce/La < 1 ("negative Ce-anomaly"), nodules have often Ce/La > 1. The difference is caused by the possibility of oxidation of trivalent Ce to the tetravalent state, leading to additional incorporation of Ce into ferromanganese mineral phases. This process is probably enhanced in areas with well-oxygenated bottom water to which nodules are exposed.

Manganese nodules from the equatorial North Pacific nodule belt (ENPN) that at present are regarded economic in terms of base metal contents, are characterized by relatively high Sb, Ba, W and Th, and they have relatively high REE contents.

GEOCHEMICAL TECHNIQUES IN INTEGRATED MARINE MINERAL EXPLORATION

Helmar Kunzendorf

Marine Mining. 8 (1989) 91 --99

The application of geochemical methods in marine mineral exploration is described. Geochemical techniques are an integral part of the search for marine minerals on the ocean floor; they include sampling, analysis, and data interpretation. Each of these steps is discussed briefly. Three marine geochemical exploration examples include placer exploration off East Australia, manganese nodule reconnaissance investigations in the Peru Basin, and the search for massive sulfides along the East Pacific Rise.

REGIONAL VARIATIONS OF REE PATTERNS IN SEDIMENTS FROM ACTIVE PLATE BOUNDARIES

H. Kunzendorf, P. Stoffers and R. Gwozdz

Marine Geology, 84 (1988) 191 - 199

About 150 sediment samples from mid-ocean ridges (East Pacific Rise, Central Indian Ocean Ridge, Carlsberg Ridge and the Red Sea) and from a back-arc spreading environment (Lau Basin) were analyzed by instrumental neutron activation. A ratio method for rare-earth elements involving a plot of elemental ratios of Ce/La and La/Yb is proposed to characterize marine sediments. In the characterization plot East Pacific Rise and Lau Basin sediments occupy distinct fields in the plot suggesting hydrothermal overprint, while sediments from the Central Indian Ocean and the Carlsberg Ridge plot into the field for normal deep-sea sediments.

THE DISTRIBUTION OF RARE EARTH ELEMENTS IN MANGANESE MICRONODULES AND SEDIMENTS FROM THE EQUATORIAL AND SOUTHWEST PACIFIC

H. Kunzendorf, R. Gwozdz, G. P. Glasby, P. Stoffers and R. M. Renner

Applied Geochemistry. 4 (1989) 183 - 191

Thirty three manganese micronodules and 38 associated sediments from selected areas in the equatorial and southwest Pacific have been analyzed for REE. Significant variations in composition of both micronodules and sediments between the areas are observed. In general, the average REE abundance in manganese nodules in a given area is higher than that of the associated micronodules but the Ce/La ratio of the micronodules is in some cases higher than that of the nodules. The average Ce/La ratio of the micronodules is always higher than that of the associated sediment but the REE abundance is lower in several cases. The Ce anomaly is dominantly positive for micronodules and negative for sediments. Negative Ce anomalies are, however, found in micronodules from the crest of the East Pacific Rise (EPR) where metallogenesis is taken place. Positive Ce anomalies occur in sediments from the Southwestern Pacific Basin between the EPR and New Zeeland. The highest Ce/La ratios of both micronodules and sediments are found in this region reflecting the well-oxidized conditions prevailing there.

COLLISION ACTIVATION OF GLUCOSINOLATE ANIONS

Gustav Bojesen, Elfinn Larsen and Vijai K. S. Shukla

Advances in Mass Spectrometry
Proceedings of the 11th International Mass Spectrometry Conference
Bordeaux 29 Aug. - 2 Sept. (1988) **11 A** and **11 B**, 1404 - 1405
Ed. by P. Longevialle
Heyden & Son Ltd., London 1989

ICP - MS, MEASUREMENT OF NICKEL

Lis Vinther Kristensen, Elfinn Larsen, and Per Solgaard

Advances in Mass Spectrometry
Proceedings of the 11th International Mass Spectrometry Conference
Bordeaux 29 Aug. - 2 Sept. (1988) **11 A** and **11 B**, 1698 - 1699
Ed. by P. Longevialle
Heyden & Son Ltd., London 1989

ICP-MS AND PIXE ANALYSIS OF ELEMENTS COLLECTED AS AIR-BORNE DUST

A. Baltzer Hansen, Elfinn Larsen, L. Vinther Kristensen, Per Solgaard, Marianne Lyngsaae, L. Valentin Hansen and Helmut Kunze

Fresenius' Zeitschrift für Analytische Chemie 334 (1989) 657

During two days under drilling operation in the Danish North Sea on the Mærsk Guardian Drilling Rig air samples from Shale Shaker House were collected onto filters. Drilling mud circulates the cuttings to the Shale Shaker House where the cuttings are separated from the mud. In the present case the mud consisted of a water slurry of $BaSO_4$ with minor amounts of additives among them chrome-lignosulfonate and chrome-lignite. For the sake of health the determination of Cr in the atmosphere of the working room was of high importance.

The filters used for collection of the air samples were Millipore cellulose acetate, 50 mm diameter and pore size 1.2 µm. The total amount collected onto the filters was determined by weighing. The filters were analyzed by PIXE (proton-induced X-ray emission). However, the detection limit for Cr is only 1 – 2% of Ba. Thus, $^1/_4$ of the filters not exposed by PIXE were dissolved completely using a microwave technique and analyzed by ICP-MS (inductively coupled plasma-mass spectrometry). Furthermore aliquots added the stable isotopes ^{135}Ba and ^{53}Cr were also analyzed by ICP-MS.

A total of 16 filters including blanks were analyzed. The total amount collected expressed as particles in the air varied from 0.05 – 1.4 mg/m^3. Several filters show an elemental distribution corresponding to that for the drilling mud. Cr was determined by ICP-MS and the maximum amount of Cr observed as 2 µg/m^3. The results from the analyses by PIXE and ICP-MS will be presented and discussed.

ON SELENOKETENES. FORMATION OF 1,3,4- SELENADIAZOLINE FROM CARBON DISELENIDE AND DIAZOALKANES

Rolf H. Berg, Niels Harrit, Elfinn Larsen and Arne Holm

Acta Chemica Scandinavica **43** (1989) 885 - 887

Di-*tert*-butyldiazomethane and carbon diselenide react in toluene at 80 °C. A compound isolated in ca. 30% yield from the mixture has been identified as the di-*tert*-butyl derivative of the hitherto unknown 2-alkylidene-2,5-dihydro-1,3,4-selenadiazoles. Further investigations indicate that the same ring system is formed upon reaction between di-*tert*-butyldiazomethane and photochemically generated *tert*-butylselenoketene. Pyrolysis in the vapor phase of the di-*tert*-butyl derivative gives rise to a mixture consisting of di-*tert*-butyl selenoketene and di-*tert*-butyl selenoketone (1:2) as well as some secondarily formed di-*tert*-butyl carbene and di-*tert*-butyl methylenecarbene.

EVALUATION OF AUTOMATED DETERMINATION OF NITROGEN - 15 BY ON-LINE COMBUSTION

Helge Egsgaard, Elfinn Larsen and Erik Steen Jensen

Analytica Chimica Acta, **226** (1989) 345 - 349

A Carlo Erba elemental Analyzer interfaced to a Finnigan MAT Delta mass spectrometer and a MAT CH-4 mass spectrometer equipped with a thermostated gas-inlet system were used in a comparative study of the $^{15}N/^{14}N$ ratios of pea powder and an ammonium sulphate standard with 0.93% and 1.34% ^{15}N, respectively. The samples were measured on-line with the Delta instrument, whereas the CH-4 instrument required a Kjeldahl digestion followed by oxidation of the ammonium ion to nitrogen in glass ampoules. The results obtained by the two methods for the ammonium standard were identical within experimental error (0.1% relative standard deviation). The pea powder gave a slightly higher ^{15}N value with the on-line method. Well-defined samples of pea powder are available for reference material purposes.

10 - ÅR MED TANDEM MASSESPEKTROMETRI

Helge Egsgaard, Elfinn Larsen and Lars Carlsen

Dansk Kemi 8 (1989) 227 - 231

Risø's Kemiafdeling fejrede den 2. december 1988 10-årsdagen for optagelsen af det første kollisionsinducerede massespektrum. Eksperimentet var samtidigt det første af sin art i Skandinavien. Introduktionen af denne teknik har i usædvanlig grad bidraget til analysefunktionens forskningspotentiale. Således har MS/MS (massespektrometri/massespektrometri) teknikken muliggjort tidstro analyse af pyrolytiske reaktioner, detaljerede studier af organiske forbindelser og af udvalgte ioniske strukturer. I det efterfølgende vil vi give en kort introduktion til MS/MS og illustrere anvendelsen af teknikken med eksempler hentet fra Kemiafdelingens grundforskning og analytisk kemiske problemstillinger. Afslutningsvis vil vi fremkomme med nogle betragtninger om denne relative nye tekniks mulige anvendelser i dansk kemisk forskning.

UNIMOLECULAR AND COLLISION INDUCED DECOMPOSITION OF PROTONATED CARBONIC ACID

Helge Egsgaard and Lars Carlsen

Advances in Mass Spectrometry
Proceedings of the 11th International Mass Spectrometry Conference
Bordeaux 29 Aug. - 2 Sept. (1988) **11 A and 11 B,** 886 - 887
Ed. by P. Longevialle
Heyden & Son Ltd., London 1989

The generation and properties of the gaseous $H_3CO_3^+$ ion has been established based on metastable ion studies as well as collision activation mass spectrometry in combination with appropriate ^2H- and ^{18}O-labelling. Theoretical studies of thermodynamical aspects were carried out applying the semi-empirical MNDO method.

NRMS -THE BRIDGE TO THE CHEMISTRY OF NEUTRAL REACTIVE INTERMEDIATES

Thomas Drewello, Helmut Schwarz, Carlito B. Lebrilla, Helena M. Florêncio, Lars Carlsen and Helge Egsgaard

Advances in Mass Spectrometry
Proceedings of the 11th International Mass Spectrometry Conference
Bordeaux 29 Aug. - 2 Sept. (1988) **11 A and 11 B,** 1016 - 1017
Ed. by P. Longevialle
Heyden & Son Ltd., London 1989

Neutralization reionization mass spectrometry (NRMS) puts a paradox into reality in that the mass spectrometric study of uncharged species becomes possible.

PROTONATED CARBONIC ACID

Helge Egsgaard and Lars Carlsen

J. Chem. Soc. Faraday Trans. 1, 85 (10) (1989) 3403 - 3411

Protonated carbonic acid is generated by a consecutive elimination of a vinyl radical and an alkene from the radical cation of dialkylcarbonates. The properties of gaseous $H_3CO_3^+$ have been established based on metastable ion studies supplementary to collision activation mass spectrometry, applying appropriate deuterium and/or ^{18}O labelling. It is concluded that protonated carbonic acid is generated as the symmetrical 'trihydroxy' species, whereas an unsymmetrical isomer is involved in the fragmentation processes, primarily leading to protonated carbon dioxide and water. The existence of an equilibrium between the symmetrical and unsymmetrical isomers can be excluded. The thermochemical aspects of the $H_3CO_3^+$ are discussed based on semiempirical MNDO calculations.

aci-NITROMETHANE - GENERATED AND CHARACTERIZED BY NEUTRALIZATION REIONIZATION MASS SPECTROMETRY

Helge Egsgaard, Lars Carlsen, Helena Flôrencio, Thomas Drewello and Helmut Schwarz

Berichte der Bunsen-Gesellschaft für physikalische Chemie 93 (1989) 76 - 80

Neutral gaseous *aci*-nitromethane has been generated and characterized by neutralization/reionization mass spectrometry (NRMS). Decomposition and isomerization patterns have been established based on studies of the corresponding nitromethane and methyl nitrite isomers in combination with appropriate deuterium labelling experiments. A comparison of the isomeric $CH_2NO(OH)$, CH_3NO_2 and CH_3ONO neutrals as well as radical cations is presented.

PROTONATED SULPHUROUS ACID

Lars Carlsen and Helge Egsgaard

Journal of Chemical Research (S) (1989) 180 - 181

ISOMERIZATION OF THE NITROETHYLENE RADICAL CATION

Helge Egsgaard and Lars Carlsen

Organic Mass Spectrometry, 24 (1989) 1031 - 1032

ANALYSIS OF LOW - PRESSURE GAS - PHASE PYROLYTIC REACTIONS BY MASS SPECTROMETRIC TECHNIQUES

Lars Carlsen

Risø - R - 545 (1989)

The report is divided into seven chapters: Chapter 1 gives a short introduction to applications of pyrolysis techniques in different areas of chemical research. Chapter 2 is devoted to the application of mass spectrometric techniques for the analysis of gas-phase reactions. The applicability of field ionization and collision activation mass spectrometry is illustrated by studies on isomerization reactions of carboxylic acid esters and the thermal decomposition of 1,2-oxathiolane. The importance of reference structures is discussed. Chapter 3 gives details on the sample/inlet systems applicable to the pyrolysis-mass spectrometry system. Chapter 4 discusses the low-pressure pyrolysis reaction, with special emphasis on reactors based on the inductive heating principle. The temperature control of the reactors is discussed in terms of a 'multitemperature' filament, as the basis for the concept of Pulse Pyrolysis. The influence of surface composition on the course of reaction is discussed, advocating for the application of gold coated surfaces to minimize surface-promoted reactions. Chapter 5 deals with low-pressure gas-kinetics on the basis of an empirical 'effective temperature' approach. Chapter 6 gives a short summary of the main achievements, which are the basis for the present report and Chapter 7 is the reference list. A Danish summary and 18 appendices, consisting of previously published papers in the period 1980-1986 are included as separate sections.

THE ROLE OF ORGANICS ON THE MIGRATION OF RADIONUCLIDES IN THE GEOSPHERE

Lars Carlsen

Nuclear Science and Technology (1989)
EUR 12024 EN

The importance of chemical and physico-chemical reactions as radioactive decay, sorption/desorption, precipitation/dissolution, filtration, redox equilibria, degradations, substitutions, hydrolysis, complex formation and colloid formation, which *a priori* can be expected to operate when radionuclides are released to the ground water and subsequently transported in the terrestrial environment is emphasized. The possible role of the operation of chemical and/or physico-chemical processes in the migration of radionuclides has recently been discussed from a theoretical point of view by Carlsen et al. [1,2]. The chemistry, possibly influencing the migration of a series of radionuclides (the "Migration Chemistry"), comprising technetium, cobalt, strontium, and the rare earth elements has recently been reported by Nilsson, Jensen, and Carlsen [3-6]. The geochemical behaviour of radionuclides, *i.e.* metal ions, has during the past decade constantly received considerable attention [7-17].

As stated in the reports on migration chemistry [3-6], complex formation with ligands present in ground water may significantly influence the migration behaviour of the radionuclides, *e.g.* owing to differences in charge for the free and complexed species. In recent years an increased awareness of the possible importance of organic ligands has developed [18-28]. The importance of a detailed knowledge of the actual species, *i.e.* correct determination of formation constants for the possibly involved complexes has been emphasized [3-6,29].

IODINE IN THE ENVIRONMENT REVISITED
AN EVALUATION OF THE CHEMICAL- AND PHYSICO CHEMICAL PROCESSES POSSIBLY CONTROLLING THE MIGRATION BEHAVIOUR OF IODINE IN THE TERRESTRIAL ENVIRONMENT

Jesper V. Christiansen and Lars Carlsen

Risø - M - 2791 (1989)

The report gives an overview of the environmental cycle of iodine, especially focussing on the possible reactions being responsible for the retention of iodine in the terrestrial environment.

During the last two decades evidence for the presence of iodine in soil as organically bound has been presented. The major part of inorganic iodine in the terrestrial environment will, under physical and chemical conditions normally prevailing, exist as iodide. No evidence for a direct reaction between iodide and organic material has been presented, whereas strong support for the engagement of microbial activity in the formation of organic iodine compounds in soil has been obtained. Incorporation of iodine in humic substances as a result of enzymatic catalysis, involving an enzyme of the peroxidase group appears reasonable. It is concluded that microbiological activity involving extracellular enzymes most probably is resonsible for the possible retention of iodine in the terrestrial environment. It is suggested that these reactions in detail should be studied experimentally.

THE MIGRATION CHEMISTRY OF NEPTUNIUM

Karen Nilsson and Lars Carlsen

Risø - M - 2792 (1989)

The chemistry of neptunium, including redox properties, complex chemistry and chemistry of neptunium in its five oxidation states, III, IV, V, VI and VII has been reviewed with special emphasis on factors, which may be of importance in controlling the environmental behavior of this element. Under environmental conditions neptunium should exist predominantly in oxidation state V in the form NpO_2^+ and to some extent also as Np(IV) in the form of Np^{4+} and Np(VI) in the form of NpO_2^{2+}, whereas the other oxidation states Np(III) and Np(VII) can not exist in the environment. However, experimental evidence is lacking as is any knowledge about the mobility of neptunium in the environment.

AN APPROACH TO SOLID STATE KINETICS

Lars Carlsen, Anders Feldthus and Peter Bo

Journal of Analytical and Applied Pyrolysis 15 (1989) 373 - 381

An approach to kinetic evaluation of pyrolytic reactions of solid material is discussed based on the assumption that the overall reaction can be described by *n*th-order kinetics, *n* possibly being fractional. The applicability of the *n*th-order kinetic approach to solid state reactions is illustrated by studies on the pyrolysis of polystyrene and coals. The possible applications to 'single-component-kinetics' is briefly discussed.

MECHANISMS AND INTERACTION PHENOMENA INFLUENCING RELEASES IN LOW- AND MEDIUM - LEVEL WASTE DISPOSAL SYSTEMS

Knud Brodersen and Karen Nilsson

Contract No. FI 1W - 0089 - DK - (B)
Annual Report 1988

MECHANISMS AND INTERACTION PHENOMENA INFLUENCING RELEASES IN LOW- AND MEDIUM - LEVEL WASTE DISPOSAL SYSTEMS

Knud Brodersen and Karen Nilsson

Contract No. FI 1W - 0089 - DK - (B)
Progress report covering the period: 1/1 to 30/6 - 1989

CHARACTERIZATION OF RADIOACTIVE WASTE FORMS VOLUME 1

K. Brodersen and K. Nilsson

Nuclear Science and Technology. EUR 12077 Progress report 1987

INDSAMLING AF DATA SAMT ANVENDELSE AF JORDBUNDSKEMIMODELLEN *ECCES* PÅ SKOVJORD

Jørgen Bille-Hansen, Mads F. Hovmand and Knud E. Brodersen

RISØ - M - 2785 (1989)

Preliminary developments are described for a project concerned with validation of the environmental effects modelling system ECCES as applied to forest soils. A description is given of two sites in Danish forest districts in Northern Zealand and Western Jutland, respectively, where a monitoring program comprising measurements of air pollution, dry and wet deposition, through-fall, litter fall and soil water composition have been in progress since 1985. The present project is a supplement to this main program.

The project has two purposes: One is to include measurements on deposition and transport of heavy metals within the forest system, since the main program is only concerned with major components. Analyses of Cd, Zn, etc. in soil water samples and in samples of the soil itself have been made using ICP-MS technique. Unfortunately even this very sensitive method was not quite sufficient to obtain significant results for these unpolluted sites.
The second purpose is to obtain additional soil data needed for the mathematical simulation of material fluxes in the forest and forest soil of major and minor components. Cation exchange capacities as functions of pH have been determined for four soil horizons at a typical site in the North Zealand forest. Distribution coefficents have been determined for the Cd/Ca system. Anion exchange capacities have been evaluated and found to be low.

Modelling of the system have not yet been attempted, but a preliminary version of the ECCES system applicable to forests has been developed.

KILDEBIDRAG TIL LUFTFORURENINGEN MED PAH OG FOREKOMSTEN AF PAH I RØGGASSEN FRA FLUID-BED ANLÆG

Torben Nielsen

RISØ - M - 2802 (1989)

Rapporten omhandler undersøgelse af forekomsten af polycycliske aromatiske kulbrinter (PAH) og basiske azaarener i atmosfæren på forskellige lokaliteter på Sjælland og i røggassen fra to fluid-bed anlæg. Trafikken var den dominerende kilde til luftforureningen i trafikerede gader. PAH-niveauerne i røggassen fra de to kulfyrede fluid-bed anlæg var moderate.

ABSOLUTE MOLAR MASS DISTRIBUTION DETERMINATION BY SIZE EXCLUSION CHROMATOGRAPHY. SYNTHESIS OF NARROW MOLAR MASS DISTRIBUTION POLYMERS.

CHARACTERIZATION OF THE MOLAR MASS DISTRIBUTION OF POLY (2-HYDROXYETHYL METHACRYLATE) BY SIZE EXCLUSION CHROMATOGRAPHY WITH COUPLED REFRACTIVE INDEX AND LOW ANGLE LASER LIGHT SCATTERING DETECTION.

Kristoffer Almdal

RISØ - M - 2787 (v.1) 1989

The absolute molar mass distribution of soluble poly(2-hydroxyethyl methacrylate) has been characterized. The characterization was accomplished by size exclusion chromatography with coupled low angle laser light scattering and refractive index detection. A new method for measurement of specific refractive index increments has been developed. The method is especially suited for mixed solvents or salt solutions. The polymer sample is equillibrated with the solvent by passage through a low exclusion molar mass size exclusion chromatography column before the measurement. The monomer 2-hydroxyethyl methacrylate has been purified. The content of both ethylene glycol dimethacrylate and methacrylic acid has been reduced to 10 ppm.

ABSOLUTE MOLAR MASS DISTRIBUTION DETERMINATION BY SIZE EXCLUSION CHROMATOGRAPHY. SYNTHESIS OF NARROW MOLAR MASS DISTRIBUTION POLYMERS.

ANIONIC POLYMERIZATION UNDER HIGH VACUUM CONDITIONS. A MANUAL FOR SYNTHESIS OF HIGH MOLAR POLYISOPRENE, POLYBUTADIENE AND POLYSTYRENE.

Kristoffer Almdal

RISØ - M - 2787 (v.2) 1989

A state of the art high vacuum line for anionic polymerization employing a turbo molecular pump has been constructed. Compared with other similar set-ups the pumping speed and thereby the efficiency of the system is much improved. Methods for the synthesis of 50 to 100 g batches of extremely high molar mass polymers of butadiene, isoprene, or styrene with a narrow molar mass distribution have been developed. The synthesized samples were characterised with respect to molar mass by size exclusion chromatography. A proton NMR chemical shift table for polyisoprenes is given. The storage and loss moduli for a polyisoprene sample with molar mass 300 000 g/mol and narrow molar mass distribution were measured over 10 decades of frequency.

PEPTIDE SYNTHESIS ON POLYSTYRENE - GRAFTED POLYETHYLENE SHEETS

Rolf H. Berg, Kristoffer Almdal, Walther Batsberg Pedersen, Arne Holm, James P. Tam and R. B. Merrifield

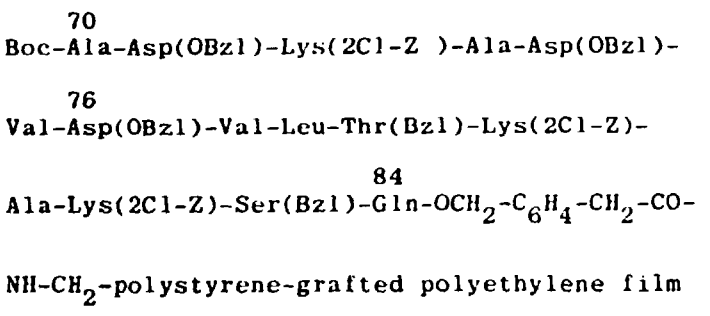
Proceedings of the 20th European Peptide Symposium
4 - 9 September, 1988, University of Tübingen
Federal Republic of Germany
Ed by Günther Jung and Ernst Bayer
New York 1989, 196 - 198

The present work concerns a novel approach (1) to solid-phase synthesis of peptides. This approach is based on the provision and use of a solid support comprising polyethylene sheets to which are grafted high molecular weight and essentially non-cross-linked polystyrene chains, which function as efficient carriers to support the synthesis of peptides. The sheets are well suited both to produce a single peptide via the "linear" solid-phase scheme or to produce multiple peptides via a rapid "parallel" scheme. The method applies to conventional solid-phase methodology and is readily adapted to both microgram and milligram scale synthesis.

LONG-CHAIN POLYSTYRENE - GRAFTED POLYETHYLENE FILM MATRIX: A NEW SUPPORT FOR SOLID - PHASE PEPTIDE SYNTHESIS

Rolf H. Berg, Kristoffer Almdal, Walther Batsberg Pedersen, Arne Holm, James P. Tam and R. B. Merrifield

The Journal of the American Chemical Society, **111** (1989) 8024 - 8026



VISCOELASTIC PROPERTIES OF BIOLOGICAL NETWORKS AND GELS

Søren Hvidt and Kurt Heller

In: Physical Networks - Polymers and Gels.
Elsevier, London (1989) 195 - 208
Ed. by W. Burchard and S. B. Ross - Murphy

The use of viscoelastic techniques in studies of structure and chain motions in biological gels and networks is discussed. Results from experiments on elastin, gelatin, fibrin, and collagen are discussed briefly as representative examples. Actin filaments regulate the structure and mechanical properties of cells. Viscoelastic properties of actin gels are interpreted as due to interpenetrating rods. Steady shear or large deformations break actin filaments and result in shear thinning and strain softening. Gelsolin, which cleaves actin filaments, can change actin gels from viscoelastic solids to viscoelastic liquids.

ENTANGLEMENT EFFECTS IN POLYMER NETWORKS AND MELTS

Søren Hvidt

In: Physical Networks - Polymers and Gels.
Elsevier, London (1989) 125 - 132
Ed. by W. Burchard and S. B. Ross - Murphy

Stress-strain data on uncrosslinked and crosslinked 1,2-Polybutadiene have been analyzed by use of the BDEW entanglement slip-link model. A consistent description of network data in different deformations and in swelling is obtained with a slip-link concentration of 280 mol/m^3 and a slippage factor of 0.05. The network slip-link contribution and results obtained from the rubber plateau region of the same uncrosslinked polymer are in excellent agreement with respect to number of slip-links and slippage factor. The main part of the network elasticity is due to fairly immobile entanglements.

UNFOLDING AND REFOLDING STUDIES OF FROG TROPOMYOSINS

S. S. Lehrer, Y. Qian and S. Hvidt

J. Biophys. 55 (1989) 202 a

ASSEMBLY OF THE NATIVE HETERODIMER OF *RANA ESCULENTA* TROPOMYOSIN BY CHAIN EXCHANGE

Sherwin S. Lehrer, Yude Qian and Søren Hvidt

Science 246 (1989) 926 - 928

Rana esculenta **tropomyosin assembles in vivo into a coiled-coil α helix from two different subunits, α and β, which are present in about equal concentrations. Although the native composition is αβ, a mixture of equal amounts of αα and ββ is produced by refolding dissociated α and β at low temperature in vitro. Refolding kinetics showed that αα formed first and was relatively stable with regard to chain exchange below approximately 20°C. Equilibration of the homodimer mixture at 30° and 34°C for long times, however, resulted in the formation of the native αβ molecule by chain exchange. Biosynthesis of αβ from separate α and β genes is, therefore, favored thermodynamically over the formation of homodimers, and biological factors need not be invoked to explain the preferred native αβ composition.**

ACTIN FILAMENTS AS A MODEL FOR RIGID POLYMER NETWORKS

Paul A. Janmey, Soren Hvidt, John D. Ferry and Thomas P. Stossel

In: Physical Networks - Polymers and Gels.
Elsevier, London (1989) 359 - 369
Ed. by W. Burchard and S. B. Ross - Murphy

We have studied the rheology of actin networks by static and dynamic shear measurements. Purified actin polymers have persistence lengths of several microns, contour lengths as much as 30 μm, and a width of 10 nm. Their length and extent of crosslinking can be regulated by two cell-derived proteins, gelsolin and actin-binding-protein (ABP). The viscosity of non-crosslinked actin filament solutions is proportional to approximately the fifth power of filament length. Introduction of ABP to solutions of short filaments results in the formation of gels that exhibit strain-hardening and rupture at larger strains. Our rheologic measurements are consistent with the interpretation that actin filaments themselves interact only sterically, and that regulation of their length and crosslinking by other proteins largely determines their rheology both in vitro and in the living cell.

THE REACTION OF HYDROXYL RADICALS AND CHLORINE ATOMS WITH SULPHUR DIOXIDE

Oliver V. Rattigan, Howard W. Sidebottom, Jack J. Treacy and Ole J. Nielsen

Proceedings of the Royal Irish Academy. **89B** (1989) 353 - 361

The rate constants for the gas-phase reaction of OH radicals and Cl atoms with sulphur dioxide have been determined at 298 ± 2K and a total pressure of approximately 1atm using a competitive rate technique. Values of the rate constants determined are k(OH + SO_2) = (6·8 ± 0·8) × 10^8 l/mol-s and k(Cl + SO_2) = (1·5 ± 0·2) × 10^7 l/mol-s. The mechanism and the importance of these reactions in the atmosphere are discussed.

AN ABSOLUTE AND RELATIVE RATE STUDY OF THE REACTION OF OH RADICALS WITH DIMETHYL SULFIDE

Ole J. Nielsen, Howard W. Sidebottom, Linda Nelson, Jack. J. Treacy and Denis J. O'Farrell

International Journal of Chemical Kinetics. **21** (1989) 1101 - 1112

The gas phase reaction of OH radicals with dimethyl sulfide (CH_3SCH_3, DMS) has been studied using both an absolute and a relative technique at 295 ± 2 K and a total pressure of 1 atm. The absolute rate technique of pulse radiolysis combined with kinetic spectroscopy was applied. Using this technique a rate constant of (3.5 ± 0.2) × 10^{-12} cm^3 $molecule^{-1}$ s^{-1} was obtained. For the relative rate method, rate constants for the reaction of OH with DMS were found to increase with increasing concentrations of added NO. These results are compared with the large body of kinetic and mechanistic data previously reported in the literature.

RATE CONSTANTS FOR THE GAS-PHASE REACTIONS OF OH RADICALS AND Cl ATOMS WITH $CH_3CH_2NO_2$, $CH_3CH_2CH_2NO_2$, $CH_3CH_2CH_2CH_2NO_2$, AND $CH_3CH_2CH_2CH_2CH_2NO_2$

Ole J. Nielsen, Howard W. Sidebottom, Denis J. O'Farrell, Michael Donlon and Jack Treacy

Chemical Physics Letters. **156** no. 4 (1989) 312 - 318

Rate constants for the reactions of OH radicals and Cl atoms with $CH_3CH_2NO_2$, $CH_3CH_2CH_2NO_2$, $CH_3CH_2CH_2CH_2NO_2$, and $CH_3CH_2CH_2CH_2CH_2NO_2$ have been determined at 295 ± 3 K and a total pressure of approximately 1 atm. The OH rate data were obtained using both the absolute rate technique of pulse radiolysis combined with kinetic spectroscopy and a conventional photolytic relative rate method. The Cl rate constants were measured using only the relative rate method. The results are discussed in terms of reactivity trends.

THE INFLUENCE OF COMPLEXATION ON RADIONUCLIDE MIGRATION: A THEORETICAL STUDY

Lars Carlsen, Ole John Nielsen and Peter Bo

Waste Management. **9** (1989) 165 - 169

The present paper describes a theoretical evaluation of the influence of complexation on metal ion (e.g., radionuclide) migration in environments containing an excess of complexing agents, that is the equilibrium between the free and the complexed metal ions can be regarded to follow pseudo first-order kinetics. It is shown that as long as the rate of interconversion between the free and complexed metal ions is rapid relative to the residence time in the system studied, the two species will migrate with the same speed, controlled by an "effective retention factor." It is clearly demonstrated that approaching zero complexation the effective retention approaches that of the more retarded species (the free metal ion), whereas the effective retention approaches that of the less retarded species (the complex) for increased complexation. The implication for the distribution of radionuclides in the terrestrial environment is discussed.

PHOTO - OXIDATION OF METHYLCHLOROFORM

O. J. Nielsen, J. Treacy, L. Nelson, I. Shanahan and H. W. Sidebottom

In: Advances in Photochemistry, 14th. International Conference on Photochemistry, Beijing, 21 - 26 Aug. (1989) 91 - 92
Ed. by Zhang Bao-wen, Tung Chen-ho and Wu Shi-kang

The reaction mechanisms for oxidation of CH_3CCl_2 and CCl_3CH_2 radicals, formed in the atmospheric degradation of CH_3CCl_3 have been elucidated. The primary oxidation products from these radicals are CH_3CClO and CCl_3CHO, respectively. Absolute rate constants for the reaction of hydroxyl radicals with CH_3CCl_3 have been measured in 1 atm of Argon at three elevated temperatures using pulse radiolysis combined with UV kinetic spectroscopy giving $k(OH+CH_3CCl_3) = (5.4\pm3)\ 10^{-12} \exp(-3570\pm890/RT)$ $cm^3molecule^{-1}s^{-1}$. A room temperature value of this rate constant of 1.3×10^{-14} $cm^3molecule^{-1}s^{-1}$ was calculated using this Arrhenius expression. A relative rate technique was utilized to provide rate data for the $OH+CH_3CCl_3$ reaction as well as the reaction of OH with the primary oxidation products. Values of the relative rate constants at 298 K are:

$k(OH+CH_3CCl_3)=(1.1\pm0.3)\times10^{-14}$
$k(OH+CH_3CClO)= (0.91\pm0.1)\times10^{-14}$
$k(OH+CCl_3CHO)=(184\pm31)\times10^{-14}$
$k(OH+CCl_2O)<0.1\times10^{-14}$

all in units of $cm^3molecule^{-1}s^{-1}$.

KINETICS AND MECHANISM FOR THE REACTION OF HYDROXYL RADICALS WITH NITROGEN CONTAINING COMPOUNDS

Michael Donlon, Denis O'Farrell, Jack Treacy, Howard Sidebottom and Ole John Nielsen

Tenth International Symposium on Gas Kinetics
University College of Swansea 24 - 29 July (1988) A 39

The interaction of peroxy organic radicals with NO and NO_2 to form nitrates and peroxynitrates is an important factor in the distribution of NO_x in the troposphere. These species provide temporary reservoirs and are expected to be involved in long range transport of NO_x. The reaction of these organonitrogen compounds with hydroxyl radicals has been suggested as an important factor in their atmospheric residence times, however, to date no mechanistic information concerning the formation and release of NO_x from these resevoirs is available. Further, there appears to be a major inconsistency between the direct measurements and relative rate techniques in the reported rate constants for OH + NO_2-containing organic compounds. It would appear that at the higher pressures pertaining in relative rate studies the measured rate constants are about an order of magnitude higher than those found in the low pressure direct determinations leading to the suggestion that as well as hydrogen atom abstraction OH radical addition also occurs to a significant extent at high pressures.

The purpose of this work was to determine relative and absolute rate data for OH radical reactions with nitroalkanes as a model for nitro compounds that may be present in the troposphere. Absolute rate data were obtained at atmospheric pressure using pulse radiolysis combined with kinetic absorption spectroscopy. Relative rate studies were carried out using a smog chamber facility having FTIR and GLC detection systems. This facility was also used to determine rate data for the reaction of chlorine atoms with the nitroalkanes.

The results of the present study indicate that at atmospheric pressure rate data for the reaction of hydroxyl radicals with nitroalkanes from both direct and relative rate experiments are in reasonable agreement. The NO_2 group substantially decreases the rate constant for H atom abstraction from groups bonded to the NO_2 group and decreases those from the groups in the β position. Similar results were found for the reaction of chlorine atoms with some deactivation occurring even at groups in the γ position. Evidence is also provided for an addition reaction of HO radicals with the nitroalkanes.

1, 1, 4, 4 - TETRAMETHYL - 1, 3 - BUTADIENE: CALCULATED AND EXPERIMENTAL RESONANCE RAMAN SPECTRA IN THE LOWEST EXCITED T_1 STATE

R. Wilbrandt, F. W. Langkilde, F. Negri and G. Orlandi

In: Proceedings of the 4th International Conference on
Time-Resolved Vibrational Spectroscopy (1989) TO 6
Ed. by T. G. Spiro and R. S. Czernuszewicz

THE STRUCTURE OF THE T_1 STATE OF 1, 3, 5 - HEXATRIENE (HT): QCFF/PI CALCULATIONS AND EXPERIMENTAL RESONANCE RAMAN SPECTRA OF E - 1, 1 - d_2 - HT AND E - 3 - d - HT

F. W. Langkilde, R. Wilbrandt, A. M. Brouwer, F. Negri and G. Orlandi

In: Proceedings of the 4th International Conference on
Time-Resolved Vibrational Spectroscopy (1989) P 14
Ed. by T. G. Spiro and R. S. Czernuszewicz

THE TRIPLET PHOTOCHEMISTRY OF E - AND Z - 1, 3, 5, - HEXATRIENE

Søren Møller, Frans W. Langkilde and Robert Wilbrandt

In: Advances in Photochemistry
Proceedings of the 14th International Conference on Photochemistry,
Beijing, Aug. 21 - 26 (1989) 192 - 193

THE LOWEST TRIPLET STATE OF 1, 3, 5 - HEXATRIENES: QUANTUM CHEMICAL FORCE FIELD CALCULATIONS AND EXPERIMENTAL RESONANCE RAMAN SPECTRA

Fabrizia Negri, Giorgio Orlandi, Albert M. Brouwer,
Frans W. Langkilde and Robert Wilbrandt

J. Chem. Phys. **90** (11) (1989) 5944 - 5963

Theoretical and Raman spectroscopic studies are presented of *E* and *Z*-1,3,5-hexatriene and their 3,4- and 2,5-dideuteriated analogs in ground and excited triplet states. The T_1 potential energy surface is calculated from extended SCF-LCAO-MO-CI theory. Energy minima and equilibrium geometries are determined in T_1. Frequencies and normal modes of vibration are calculated for the minima of the T_1 and S_0 states. Energies of higher triplet levels are computed and oscillator strengths for the transitions from T_1 to T_n are determined. The displacements in equilibrium geometries between the T_1 and the T_n level corresponding to the strongest $T_1 \rightarrow T_n$ transitions are calculated and are used to estimate the intensities of the resonance Raman spectra of the T_1 state under the assumption of a predominant Franck–Condon scattering mechanism. The results indicate that the planar *E* and *Z* forms of hexatriene and its analogs are the only ones contributing substantially to the $T_1 \rightarrow T_n$ absorption and the T_1 resonance Raman spectra found in the present experiments. The existence of a twisted form in the T_1 state cannot be ruled out, but its contribution to the resonance Raman spectra corresponding to an electronic $T_1 \rightarrow T_n$ transition around 315 nm is likely to be much weaker than that of the *E* or *Z* forms. Satisfactory agreement is found between the calculated and experimentally determined resonance Raman spectra. An assignment is obtained for the experimentally determined vibrational modes in T_1. The theoretical results indicate a substantial rotation of normal modes from S_0 to T_1.

VIBRATIONAL SPECTRA OF 1, 3, 5 - HEXATRIENE AND METHYLATED DERIVATIVES - II. THE COUPLING PATTERN FOR LATERAL METHYLATION

Frans W. Langkilde, Bjarne Amstrup, Robert Wilbrandt and Albert M. Brouwer

Spectrochimica Acta **45A** No.9 (1989) 883 - 903

The vibrational spectra of *E*-2-methyl-hexatriene (E2MH), 4-*d*-*E*-2-methyl-hexatriene (dE2MH), and *E*-3-methyl-hexatriene (E3MH) were measured and interpreted using semi-empirical QCFF/π calculations and empirical valence force field (VFF) calculations. The vibrational patterns of E2MH and E3MH are discussed on the basis of the VFF calculations. It is found that the vibrational pattern of E3MH resembles that of *E*-1,3,5-hexatriene whose normal modes to a high degree can be described by global symmetry coordinates, whereas the pattern of E2MH resembles that of isoprene whose normal modes are more influenced by local symmetry coordinates. The effect of steric hindrance on methyl group conformation and the coupling of the methyl group vibrations with those of the polyene chain are discussed.

SENSITIZED PHOTOISOMERIZATION OF *ALL-TRANS*- AND 11 - *CIS* - RETINAL

Niels - Henrik Jensen, Robert Wilbrandt and René V. Benasson

Journal of the American Chemical Society **111** (1989) 7877 - 7888

The photoisomerization of *all-trans*-retinal (all-trans) and 11-*cis*-retinal (11-cis) sensitized by a range of sensitizers (porphyrins, Zn-porphyrins, naphthacene and a Zn-phthalocyanine) with varying triplet energies above and below the vertical triplet energy of *all-trans*-retinal (E_T = 149 kJ/mol) has been investigated by continuous illumination and HPLC analysis of the products. The composition of the photostationary states, the relative isomerization quantum yields of all-trans and 11-cis, and the primary product ratios are reported. One photon–one bond isomerizations are dominant. With *Zn*-TPP as sensitizer it is shown that 11-cis and possibly all-trans undergoes one photon–two bond isomerizations as well. The quantum yields of photoisomerization of 11-cis sensitized by biphenyl (E_T = 275 kJ/mol) and anthracene (E_T = 178 kJ/mol) were found to be identical. Absolute measurements allowed evaluation of the overall triplet isomerization quantum yield of 11-cis, Φ^T_{iso}(11-cis→) = 1.0 ± 0.2, from which the corresponding quantity for all-trans, Φ^T_{iso}(trans →) = 0.15 ± 0.05, was obtained. The overall photoisomerization quantum yield of 11-cis with direct excitation at 254 nm was determined as Φ^d_{iso}(11-cis→) = 0.42 ± 0.05 assuming all-trans and 13-cis to be the primary products. Quenching rate constants of several of the sensitizer triplet states by retinal were measured by laser flash photolysis. Possible mechanisms that could account for the experimental results are discussed, and it is concluded that the photoisomerizations most likely involve the retinal triplet states as intermediates. Within this model the observed sensitizer triplet energy dependence of the primary product ratios suggests that the triplet states of the different retinal isomers are different mixtures of triplet excited species, and that the composition of these mixtures depends on the starting isomer as well as on the sensitizer triplet energy for energies below the vertical triplet energy of *all-trans*-retinal. In the light of a review of the existing literature on the direct and the sensitized photoisomerization of retinals these conclusions suggest substantial corrections to the accepted picture of retinal photochemistry.

UV SPECTRUM OF CD_2OD AND ITS REACTIONS WITH O_2, NO AND NO_2

Palle Pagsberg, Jette Munk, Christopher Anastasi and Victoria Simpson

Chemical Physics Letters 157 No.3 (1989) 271 - 276

The ultraviolet spectrum of CD_2OD has been measured between 210 and 300 nm using a pulse radiolysis–absorption method. The spectrum consists of a series of vibronic transitions with the (0, 0) electronic transitions to 3s and 3p Rydberg states identified at 284.7 and 244.0 nm. Several bimolecular reaction rates have been measured by monitoring the CD_2OD absorption at 284.7 nm. A rate constant of $(4.9 \pm 0.7) \times 10^{-11}$ cm^3 molecule^{-1} s^{-1} has been measured for the mutual reaction of CD_2OD, and values of $(0.97 \pm 0.04) \times 10^{-11}$, $(2.3 \pm 0.3) \times 10^{-11}$ and $(1.8 \pm 0.5) \times 10^{-11}$ cm^3 molecule^{-1} s^{-1} obtained for reactions with O_2, NO and NO_2, respectively. Pathways for the latter three reactions are discussed.

REACTION OF CH_2OH WITH O_2, NO, AND NO_2 AT ROOM TEMPERATURE

Palle Pagsberg, Jette Munk, Christopher Anastasi and Victoria J. Simpson

The Journal of Physical Chemistry 93 (1989) 5162 - 5165

The reaction of CH_2OH with O_2, NO, and NO_2 has been studied using pulse radiolysis to generate the radicals and ultraviolet absorption to observe the kinetics. Rate constant values of $(0.88 \pm 0.02) \times 10^{-11}$, $(2.5 \pm 0.02) \times 10^{-11}$, and $(2.3 \pm 0.4) \times 10^{-11}$ cm^3 molecule^{-1} s^{-1} have been measured at room temperature and 1 atm pressure for the O_2, NO, and NO_2 reactions, respectively. Absorptions due to long-lived or stable products were observed in the same spectral region. A simple analysis of these observations suggests that formation of an adduct may dominate in the reaction of CH_2OH with NO and NO_2 but that this process accounts for only a minor route in the O_2 reaction.

THE REACTION OF CH_2OH WITH O_2, NO AND NO_2

C. Anastasi, J. Munk, P. Pagsberg and V. J. Simpson

Tenth International Symposium on Gas Kinetics
University College of Swansea 24 - 29 July (1988) A 40

SPECTRUM AND KINETICS OF A QO_2H SPECIES

C. Anastasi, P. Genske, P. Pagsberg and M. Poxon

Tenth International Symposium on Gas Kinetics
University College of Swansea 24 - 29 July (1988) B. 20

MEASUREMENTS WITH ALANINE AND FILM DOSIMETERS FOR INDUSTRIAL 10 MeV ELECTRON REFERENCE DOSIMETRY

A. Miller, A. Kovàcs, A. Wieser and D. F. Regulla

Appl. Radiat. Isot. 40 No. 10 - 12 (1989) 967 - 969
Int. J. Radiat. Appl. Instrum., Part A

Alanine and radiochromic film dosimeters were irradiated with absorbed doses from 3 to 10 kGy at a 10 MeV electron accelerator under typical radiation processing conditions. The nominal doses were measured by graphite calorimeters and the dosimeters were irradiated in graphite phantoms. The dosimeters were calibrated by irradiation with ^{60}Co photons.

The ratios of calorimeter to film and alanine dosimeter readings were generally within 0.99 ± 0.01 for 10 mm phantoms, but larger differences were observed for 20 mm phantoms. The discrepancies may be due to uncertainties in irradiation geometry, or in the stopping power ratios applied.

DOSIMETRY FOR THE APPROVAL OF FOOD IRRADIATION PROCESSES

A. Miller and K. H. Chadwick

Radiat. Phys. Chem. 34 No. 6 (1989) 999 - 1004
Int. J. Radiat. Appl. Instrum., Part C

APPLICATION OF CALORIMETERS FOR ROUTINE AND REFERENCE DOSIMETRY AT 4 - 10 MeV INDUSTRIAL ELECTRON ACCELERATORS

Arne Miller and Andras Kovacs

Radiat. Phys. Chem. 35 (1989) 774 - 778

Calorimeters are indispensable for characterization, validation and routine checking of the performance of industrial electron accelerators. This paper describes how calorimetry can establish traceability to primary standards, how routine dosimeters are calibrated by means of calorimetry, and how nominal doses are documented by calorimetry during validation exercises and during daily operation. Construction and calibration of the calorimeters are described, and data on the precision and accuracy are given.

DOSIMETRY FOR RADIATION PROCESSING

W. L. McLaughlin, A. W. Boyd, K. H. Chadwick, J. C. McDonald and A. Miller

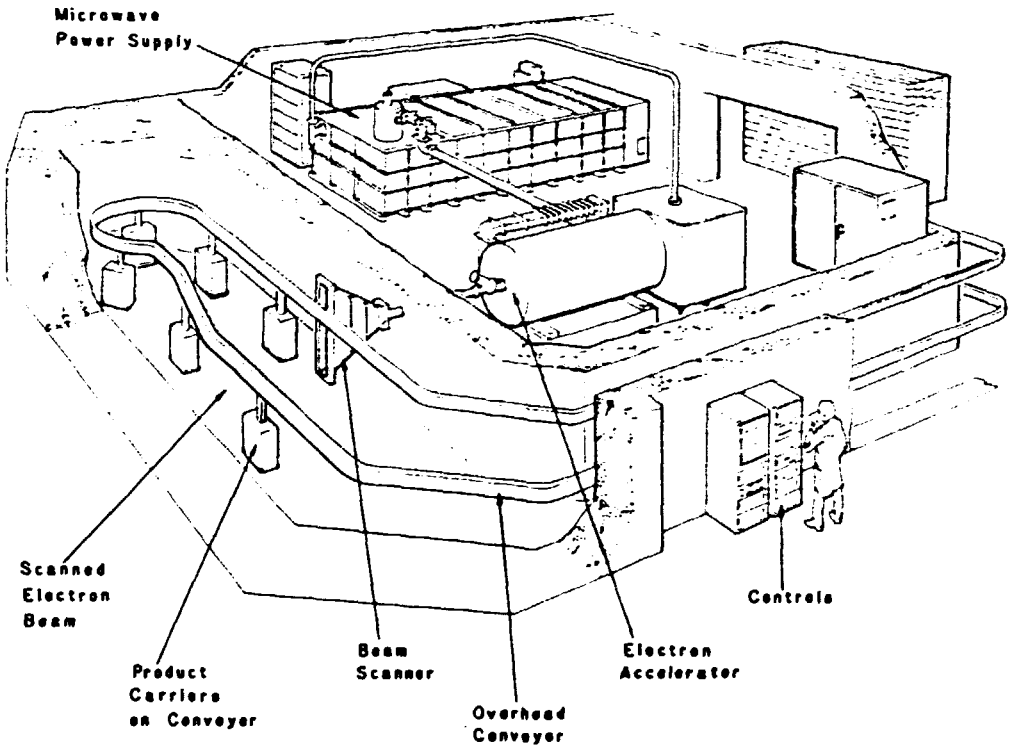
Taylor & Francis, London 1989

The use of accurate and precise radiation dosimetry to control the food irradiation process for regulatory purposes is discussed. The various procedures required to establish a thorough dosimetric control, such as commissioning the irradiation facility, process validation and routine control are described. It is concluded that, coupled with an administrative inventory control, dosimetry can provide the guarantee that the process has been correctly applied and regulatory release of irradiated food can be based on accurate and reproducible absorbed dose measurements.

STRÅLING - ET VÆRKTØJ I INDUSTRI OG SYGDOMSBEKÆMPELSE

Arne Miller

Fysik - Kemi 3 (1989) 20 - 22



Procesbestråling, f.eks. sterilisation af hospitalsudstyr, foregår på store Kobolt-60 anlæg eller som her på en elektronaccelerator. Denne maskine sender en stråle af elektroner mod produkterne, der passerer forbi strålingszonen ved hjælp af et transportbånd.

DOSIMETRY FOR INDUSTRIAL ELECTRON BEAM IRRADIATION

Arne Miller

IAEA Technical Contract 4748 / R1 / RB
Progress report for the period 15 dec. 1988 - 14 dec. 1989

INVESTIGATION OF ALANINE AS AN ACCIDENT DOSIMETER AND INTERPRETATION OF DOSE - EFFECT RELATIONSHIPS BY MODEL DESCRIPTION

Johnny W. Hansen and K. Sehested

Final report 1986 - 1988, 143 - 153
Commission of the European Communities, Brüssels, 1989 (EUR-12064)

ESR DOSIMETRY IN CALIBRATION INTERCOMPARISONS WITH HIGH - ENERGY PHOTONS AND ELECTRONS

K. J. Olsen, J. W. Hansen and M. P. R. Waligórski

Appl. Radiat. Isot. 40 No. 10 - 12 (1989) 985 - 988
Int. J. Radiat. Appl. Instrum., Part A

When alanine is exposed to radiation, stable free radicals are produced which may be measured by electron spin resonance (ESR) spectroscopy. Our dosimeters consist of L-α-alanine mixed with 5% polyvinyl pyrrolidone, compacted in the shape of 2-mm thick cylinders of 4.5 mm diameter. The alanine dosimeters were exposed to 0.25 to 16-MV_x x-ray beams and 6 to 20-MeV electron beams and measured at Risø National Laboratory. Doses were determined by comparison with alanine dosimeters exposed to ^{60}Co γ-rays calibrated with Fricke dosimetry. At absorbed doses above 10 Gy, the standard deviation for the dose measurements was 1%. Dosimetry comparisons better than 2% at the 95% confidence level are possible. The dosimeters are easy to handle, robust, and cheap, and may be read repeatedly. Fading after 100 Gy of ^{60}Co γ-rays and Linac-produced x-ray and electron beams is less than 2 and 6% in 4 years, respectively. Alanine dosimeters are useful for dosimetry comparisons both for photons and electrons, and the negligible fading make them ideal for documentation of patient doses in radiation therapy.

MEASUREMENT OF DOSE RATE FROM $^{106}Ru/^{106}Rh$ OPHTHALMIC APPLICATORS BY MEANS OF ALANINE - POLYMER FOILS

P. Hjortenberg, J. W. Hansen and M. Wille

Appl. Radiat. Isot. 40 No. 10 - 12 (1989) 997 - 1001
Int. J. Radiat. Appl. Instrum., Part A

Ophthalmic applicators are used in radiotherapy for the treatment of malignant choroidal melanomas. The applicators are positioned on the eye at the base of the tumor for a period of a few days up to 2 weeks. They are commercially available in the form of caps of a spherical radius of 12 or 13 mm. Two or three fixing lugs are used for suturing the applicator to the eye. The applicators are made of silver. The active layer is covered with 0.1 mm silver in the concave direction, and 0.9 mm silver in the convex direction. The β-radiation emitted from the concave side may be used for treatment, to a depth up to 5 mm. Measurements of dose rate by means of ESR/alanine dosimetry and TLD are described. It is concluded that ESR dosimetry and TLD are well suited for this application.

ON THE PREDICTION OF DECAY IN RADICAL CONCENTRATION IN L - ALPHA - ALANINE FOLLOWING HIGH - LET EXPOSURES

J. W. Hansen and K. J. Olsen

Gesellschaft für Schwerionenforschung
Annual Scientific Report (1988) Darmstadt, FRG. GSI - 89 - 1
ISSN 0174 - 0814

PREDICTING DECAY IN FREE - RADICAL CONCENTRATION IN L - ALPHA - ALANINE FOLLOWING HIGH -LET RADIATION EXPOSURES

J. W. Hansen and K. J. Olsen

Appl. Radiat. Isot. 40 No. 10 - 12 (1989) 935 - 939
Int. J. Radiat. Appl. Instrum. Part A

Efforts have been made to develop a model that will predict time-dependent decay in radiation-induced free-radical concentration in L-α-alanine following heavy-charged-particle exposures. The decay rate depends on radiation quality, dose and dose-rate. For low doses, the decay-rate is approx. 0.5 and 1.5% per year following ^{60}Co γ-ray exposures and Linac-produced x-ray or electron exposures. Decay rates, however, have been found to increase as measured from low average doses, sparse single tracks, of heavy charged particles. We have compared measured decay after exposures to low average doses from high-LET particles with predicted decay calculated as function of particle velocity and charge and detector parameters. The predicted decay is obtained by folding measured decay after Linac-produced electron exposures of very high doses into the calculated dose distribution around the heavy ion's path. Preliminary results show agreement between the experimental data and results obtained from this model, within the experimental uncertainty.

INTERCOMPARISON OF GAMMA RAY, X RAY, AND FAST NEUTRON DOSIMETRY USING ALANINE DETECTORS

J. W. Hansen, M. P. R. Waligorski and E. Byrski

Radiation Protection Dosimetry 27 No. 2 (1989) 85 - 92

Alanine detectors manufactured in Poland and in Denmark were intercompared by exposing them to ^{60}Co γ ray beams at the centre of Oncology, Cracow, and at Risø National Laboratory. Both types of detectors were exposed to a beam of 250 kVp X rays and to a cyclotron-produced fast neutron beam of mean energy 5.6 MeV at the Institute of Nuclear Physics in Cracow, and measured using ESR spectrometry at Cracow and at Risø. The typical accuracy with which Polish and Danish alanine detectors can measure gamma doses is about 2%. Measurements of effectiveness, relative to ^{60}Co γ rays, of the alanine detector yielded: for 250 kVp X rays 0.82 ± 0.06 (Polish detectors) and 0.82 ± 0.03 (Danish detectors); for fast neutrons 0.63 ± 0.04 (Polish detectors) and 0.62 ± 0.03 (Danish detectors), where all sources of error are included.

EXPERIMENTAL AND THEORETICAL INVESTIGATIONS OF THE ALANINE DOSEMETER AS A PERSONAL ACCIDENT DOSEMETER IN MIXED FIELD RADIATION

Johnny W. Hansen and Kjeld J. Olsen

Final Report to the Commission of the European Communities
Radiation Protection Program.
Project no.: B16 - A - 028 - DK
Risø, January 1989

THE LIDAR THOMSON SCATTERING DIAGNOSTIC ON JET

H. Salzmann, J. Bundgaard, A. Gadd, C. Gowers, V. Gusev,
K. B. Hansen, K. Hirsch, P. Nielsen, K. Reed, C. Schrödter and K. Weisberg

JET - R (89) 07 (1989)

By combining the time-of-flight or LIDAR principle with a Thomson backscatter diagnostic, spatial profiles of the electron temperature and density can be measured with a single set of detectors for all spatial points. This approach considerably simplifies the collection optics required for measuring a spatial profile. The technique was realised for the first time on the JET tokamak and has been in routine operation since July 1987. A ruby laser (3 J pulse energy, 300 ps pulse duration, 0.5 Hz repetition rate) together with a 700 MHz bandwidth detection and registration system yields a spatial resolution of about 12 cm. A large filter spectrometer with 6 spectral channels covering the wavelength range 400 - 800 nm gives a dynamic range of the temperature measurements of 0.3-20 keV. The stray light problem in the backscatter geometry is overcome by spectral discrimination and effective gating of the MCP photomultipliers. A high rejection ruby notch filter in the spectral channel containing the laser wavelength allows calibration of the vignetting along the line of sight by means of Raman scattering, thus enabling the measurement of density profiles. The low level of plasma background signal due to the short integration time for an individual spatial point yields low statistical errors ($\Delta T_e/T_e \approx 6\ \%, \Delta n_e/n_e \approx 4\ \%$ at $T_e = 6$ keV, $n_e = 3 \times 10^{19}$ m^{-3}). Goodness-of-fit tests indicate that the systematic errors are within the same limits. The system is described and examples of measurements are given and compared with the results of other diagnostics.

ELECTRONICS FOR MICROCHANNEL PHOTOMULTIPLIERS IN THE LIDAR THOMSON SCATTERING DIAGNOSTIC ON JET

J. Bundgaard, K. B. Hansen and K. -V. Weisberg

Review of Scientific Instruments, 60 No. 10 Oct. (1989) 3265 - 3269

The electronics for the microchannel plate photomultiplier tubes used in the LIDAR (Light Detection and Ranging) Thomson scattering diagnostic on the JET tokamak are described. It is shown how the microchannel plate photomultiplier tubes are gated with a very small coupling between gate signal and output, and how ~ 300 V transient pulses with rise times of 230 ps are clipped to safe levels of ~ 40 V.

RADIOLYSIS OF REACTOR WATER: REACTION OF OH RADICALS WITH O_2^-

H. Christensen, K. Sehested and E. Bjergbakke

Water Chemistry of Nuclear Reactor Systems 5. BNES, London (1989) 141 - 144

A programme with the objective of studying the radiation chemistry of water at the operating temperature of a power reactor, is being undertaken. In the present investigation the rate constant of the reaction between OH and O_2^- radicals has been determined as a function of temperature using the technique of competition kinetics: OH radicals, produced by a pulse of electrons, react either with O_2^- radicals or hydrogen. Using computer fitting, the best agreement between the calculated and measured yields of O_2^- is obtained. The rate constants at 20 and 285 ^{o}C are $(1.0\pm0.1)\cdot10^{10}$ and $(2.9\pm0.5)\cdot10^{11}$ $dm^3\cdot mol^{-1}\cdot s^{-1}$ respectively. The activation energy is 17.6 ± 1.3 $kJ\cdot mol^{-1}$ (4.2 ± 0.3 $kcal\cdot mol^{-1}$).

RADIOLYSIS OF GROUND WATER: INFLUENCE OF CARBONATE AND CHLORIDE ON HYDROGEN PEROXIDE PRODUCTION

T. E. Eriksen, P. Ndalamba, H. Christensen and E. Bjergbakke

Journal of Radioanalytical and Nuclear Chemistry,
Articles, 132 No. 1 (1989) 19 - 35

and in:

SKB Technical Report, 88 - 22 (1988)

Small volumes of aqueous solutions have been subjected to α-radiation from a ^{241}Am source. The irradiated solution was separated from the bulk solution by a glass filter serving as a diffusion barrier. The H_2O_2 concentration in the bulk solution was monitored by a chemiluminescence technique and the overall production of oxidizing species (H_2O_2/O_2) in irradiated ground water was studied by measuring the Fe^{2+}-consumption in ground water initially containing $2 \cdot 10^{-6}$ mol dm^{-3} Fe^{2+}. H_2O_2 yields calculated using the computer program CHEMSIMUL are in fair agreement with experimental yields for "pure" water (pH 8) and aqueous methanol solutions (pH 5). Experimentally $G(H_2O_2) = 1.06 \pm 0.1$ was obtained in "pure" water. In solutions containing $2 \cdot 10^{-3}$ mol·dm^{-3} HCO_3^- and in ground water $G(H_2O_2)$ decreased to 0.69 ± 0.03. A corresponding decrease in $G(H_2O_2)$ was not found in the calculations. The agreement between measured and calculated Fe^{2+} consumption is fair when slow oxidative reactions in the bulk solutions are taken into account.

RADIOLYTIC PRODUCTS IN WATERS

PART I: COMPUTER SIMULATION OF SOME RADIOLYTIC PROCESSES IN THE LABORATORY

E. Bjergbakke, Z. D. Dragenic', K. Sehested and I. G. Dragenic'

Radiochimica Acta 48 (1989) 65 - 71

We survey the products H_2O_2 formed in water and aqueous solutions due to the decomposition induced by ionizing radiation. The results are obtained by computer simulations based on the standard model of water radiolysis, experimental data on the free radicals involved, their radiation chemical yields and the rate constants of their reactions. The formation of H_2O_2 and other radiolytic products is given for several cases, which are relevant to the use of water as solvent in radiochemistry and nuclear technology. The solutes chosen are representatives of common impurities appearing in micro- or submicromole concentrations, and the dose rate is of the order of magnitude commonly used in laboratory work.

THE DICHROMATE DOSIMETER: A PULSE - RADIOLYSIS STUDY

Peter H. G. Sharpe and Knud Sehested

Radiat. Phys. Chem. 34 No. 5 (1989) 763 - 768
Int. J. Radiat. Appl. Instrum. Part C

A pulse-radiolysis study has been made of the dichromate dosimeter and an outline mechanism proposed. The following rate constants have been determined:

$OH + Cr(V) \rightarrow Cr(VI) + OH^- \; k = (1.5 \pm 0.5) \times 10^9\ dm^3 mol^{-1} s^{-1}$;
$Ag(II) + Cr(V) \rightarrow Ag(I) + Cr(VI) \; k = (5.8 \pm 0.6) \times 10^7\ dm^3 mol^{-1} s^{-1}$;
$HO_2 + Ag(II) \rightarrow H^+ + O_2 + Ag(I) \; k = (1.7 \pm 0.2) \times 10^9\ dm^3 mol^{-1} s^{-1}$;
$HO_2 + Cr(VI) \rightarrow Complex\ 1 \; k = 1 \times 10^5\ dm^3 mol^{-1} s^{-1}$;
$Complex\ 1 \rightarrow Cr(V) \; k = 0.25\ s^{-1}$;
$H_2O_2 + Cr(VI) \rightarrow Complex\ 2 \; k = 1 \times 10^3\ dm^3 mol^{-1} s^{-1}$;
$Complex\ 2 \rightarrow Cr(IV) \; k = 0.25\ s^{-1}$;
$Ag(II) + H_2O_2 \rightarrow Ag(I) + HO_2 \; k = (4.5 \pm 0.5) \times 10^7\ dm^3 mol^{-1} s^{-1}$.

ARSENIC (IV). A PULSE - RADIOLYSIS STUDY

U. K. Kläning, Benon H. J. Bielski and K. Sehested

Inorganic Chemistry, **28** (1989) 2717 - 2724

Four As(IV) species assumed to be $As(OH)_4$ and $HAsO_3^-$ and the corresponding bases $As(OH)_3O^-$ and AsO_3^{2-} (pK_a = 7.38 and 7.81, respectively) were observed by the pulse-radiolysis technique in aqueous arsenious acid, arsenite, and arsenate solutions. $As(OH)_4$ and $As(OH)_3O^-$ were observed in acid and weakly alkaline solution by the reaction of arsenious acid or arsenite with OH. $HAsO_3^-$ and/or AsO_3^{2-} are formed by the reaction of e^-_{aq} with $H_2AsO_4^-$ and $HAsO_4^{2-}$; AsO_3^{2-} is formed by the reaction of arsenite with O^- in strongly alkaline solution and by the reaction of arsenite with the carbonate radical anion CO_3^-. $As(OH)_4$ and $As(OH)_3O^-$ convert into $HAsO_3^-$ and AsO_3^{2-} by general-base-catalyzed reactions. In acid solution an equilibrium between $As(OH)_4$ and $HAsO_3^-$ is observed. The kinetics of dehydration of $As(OH)_4$ suggest a slow dehydration step catalyzed by H^+ followed by protolysis:

$$As(OH)_4 \underset{k_r}{\overset{k_f}{\rightleftharpoons}} H_2AsO_3 + H_2O \cdots HAsO_3^- + H_2O + H^+$$

$k_f/k_r \sim 10^{-3}$–10^{-2}; $k_f = 2.4 \times 10^4 + 3.8 \times 10^8[H^+]\ s^{-1}$. The equilibrium constant for the overall reaction is 1.4×10^{-4}; the standard enthalpy of reaction is 10.4 kJ mol^{-1}. The energy and the entropy of activation for the uncatalyzed and the H^+-catalyzed dehydration of $As(OH)_4$ are 23 kJ mol^{-1} and −93 J mol^{-1} K^{-1} and 25 kJ mol^{-1} and −6 J mol^{-1} K^{-1}, respectively. By comparison with activation parameters of other dehydration–hydration processes, these values are taken to suggest a cyclic transition state containing an extra water molecule. While $As(OH)_4$ and $As(OH)_3O^-$ react with O_2 to yield directly HO_2 and O_2^-, $HAsO_3^-$ and AsO_3^{2-} react with O_2 with formation of a relatively stable complex that subsequently decomposes to HO_2 or O_2^- in reactions catalyzed by H^+ and OH^-. The various As(IV) species disappear in second-order reactions with rate constants ranging from 2×10^7 to 2×10^9 dm^3 mol^{-1} s^{-1}. As(IV) species are both very strong oxidants and reductants. (Estimates for the standard reduction potentials $As(OH)_4 + e^- + H^+ \rightarrow As(OH)_3 + H_2O$ and $H_3AsO_4 + e^- + H^+ \rightarrow As(OH)_4$ are 2.4 and −1.2 V, respectively.)

TEMPERATURE DEPENDENCE OF INTRAMOLECULAR ELECTRON TRANSFER AS A PROBE FOR PREDENATURATIONAL CHANGES IN LYSOZYME

Krzysztof Bobrowski, Jerzy Holcman and Kazimierz Lech Wierzchowski

Free Rad. Res. Comms. **6** No. 4 (1989) 235 - 241

Intramolecular electron transfer in hen egg-white lysozyme between tryptophan and tyrosine units was investigated by means of pulse radiolysis in the temperature range 288–333 K. An Arrhenius plot for the kinetics of this process shows a sharp break at ~ 303 K (30°C) compatible with the trend noted earlier (cf. P. Jolles, *et al. BBA*, **491**, 354, (1977)) on the Arrhenius plot for kinetics of bacterial substrate digestion by lysozyme. The departure from linearity of the Arrhenius plot for intramolecular electron transfer is interpreted in terms of local intralobe fluctuations of the native structure of lysozyme. It is suggested that such an approach can be useful for probing predenaturational changes in proteins.

FORMATION AND STABILITY OF INTRAMOLECULAR THREE - ELECTRON S ∴ N, S ∴ S, and S ∴ O BONDS IN ONE - ELECTRON - OXIDIZED SIMPLE METHIONINE PEPTIDES. PULSE RADIOLYSIS STUDY

K. Bobrowski and J. Holcman

Journal of Physical Chemistry, 93 (1989) 6381 - 6387

Intramolecular sulfur–sulfur $(S.\therefore S)^+$ and sulfur–nitrogen $(S.\therefore N)^+$ three-electron-bonded radical cations and sulfur–oxygen (S.∴O) radicals have been generated in aqueous solutions of some simple di-, tri-, and tetrapeptides containing methionine units due to oxidation by hydroxyl radicals under pulse radiolysis conditions. All these transient species are formed at the diffusion-controlled rate ($k \geq 10^{10}$ dm^3 mol^{-1} s^{-1}), and they exhibit optical absorptions with the maxima at 390 nm (S.∴N- and S.∴O-bonded species) and at 490 nm (S.∴S-bonded species) with extinction coefficients of 5000–7000 dm^3 mol^{-1} cm^{-1}. In slightly acidic solutions of tri- and tetrapeptides, a protolytic equilibrium between S.∴O- and S.∴S-bonded species was observed. The position of this equilibrium shifts by approximately 2 pK units when going from L-Met-Gly-L-Met (pK = 3.05) to L-Met-Gly-L-Met-L-Met (pK = 5.15). Conversion of the S.∴O-bonded species into the S.∴S-bonded species proceeds via kinetically distinct [H$^+$]-dependent ($k = 10^7$–10^9 dm^3 mol^{-1} s^{-1}) and [H$^+$]-independent ($k \simeq 10^4$ s^{-1}) routes. In the pH range 6.0–9.0, a pH- and buffer-concentration-independent conversion of the 490-nm into the 390-nm absorption band was observed. This fast process ($k > 10^5$ s^{-1}) is consistent with the conversion of the S.∴S-bonded species into the S.∴N-bonded species.

THE INTERACTION BETWEEN Cu (I) SUPEROXIDE DISMUTASE AND HYDROGEN PEROXIDE

Diane E. Cabelli, Deborah Allen, Benon H. J. Bielski and Jerzy Holcman

The Journal of Biological Chemistry, 264 No. 17 (1989) 9967 - 9971

The interaction between superoxide dismutase (SOD) and peroxide, under anaerobic conditions in the presence of an OH radical scavenger, formate, and an indicator, nitro blue tetrazolium, involves five reactions and an equilibrium:

$$SOD\text{-}Cu^{2+} + H_2O_2 \rightleftharpoons SOD\text{-}Cu^{+} + O_2^{\cdot-} + 2H^{+} \quad (1, -1)$$

$$SOD\text{-}Cu^{2+} + O_2^{\cdot-} \rightarrow SOD\text{-}Cu^{+} + O_2 \quad (2)$$

$$SOD\text{-}Cu^{+} + HO_2^{\cdot} + H^{+} \rightarrow SOD\text{-}Cu^{2+}\text{-}OH + OH^{-} \quad (3a)$$

$$SOD\text{-}Cu^{2+}\text{-}OH + HCO_3^{-} \rightarrow SOD\text{-}Cu^{2+} + H_2O + CO_3^{\cdot-} \quad (4)$$

$$CO_3^{\cdot-} + NBT^{2+} \rightarrow CO_2 + NBT^{+\cdot} \quad (5)$$

$$NBT^{+\cdot} + NBT^{+\cdot} \rightarrow NBT^{2+} + MF^{+} \quad (6)$$

Reaction 3 occurs at a rate that is proportional to both peroxide and enzyme with no kinetic evidence for any intermediate peroxide-enzyme complex. Rate studies as a function of pH corroborate previously published work (Fuchs, H. J. R., and Borders, C. L., Jr. (1983) *Biochem Biophys. Res. Commun.* 116, 1107–1113; Blech, D. M., and Borders, C. L., Jr. (1983) *Arch. Biochem. Biophys.* 224, 579–586) suggesting that HO_2^{-}, and not H_2O_2, is the active species in this system: $k(HO_2^{-}$ + superoxide dismutase-$Cu^{+}) = 2.6 \times 10^{7}\ M^{-1}\ s^{-1}$. Evidence is presented which suggests that HO_2^{-}, like $O_2^{\cdot-}$, reacts at rates that are affected by the electrostatic forces of the enzyme.

RECOVERY OF GOLD FROM A GOLD - THIOUREA - LOADED ION EXCHANGER

A. B. Bjerre and E. Sørensen

Trans. Instn Min. Metall. (Sec. C : Mineral Process. Extr. Metall.) 98
January - April 1989 84 - 87

The use of a strong-acid cation exchanger for the recovery of gold from a thiourea leach solution was investigated. It is well known that the gold–thiourea complex is readily adsorbed on a cation exchanger. The problems lie in the purification and elution of the gold so as fully to regenerate the ion exchanger. The most common impurities are copper and iron, which are stripped by $HNO_3 + H_2O_2$ and by NH_4NO_3, respectively.

The gold–thiourea complex is retained very firmly by the ion exchanger and refuses to be displaced by other ions. The desorption is, therefore, brought about by a ligand-exchange process with the use of thiosulphate, which yields the complex anion $AuS_2O_3^-$. Since the ion exchanger has no affinity for anions, the $AuS_2O_3^-$ will leave the column immediately. It is important for successful elution that pH is kept within the

ATMOSFÆRISK TUNGMETAL DEPOSITION I DANMARK, ISLAND, GRØNLAND OG NORDTYSKLAND 1985 - MONITERET VED ANALYSER AF MOS

Kim Pilegaard and Lennart Rasmussen

Risø - M - 2754 Marts (1989)

Den atmosfæriske deposition af tungmetaller i de nordiske lande blev i 1985 undersøgt ved brug af mos som monitororganisme. Den foreliggende rapport giver en detaljeret gennemgang af resultaterne for Danmark, Grønland, Island og Nordtyskland. Prøver af mos blev indsamlet til analyse for arsen, cadmium, kobolt, kobber, jern, nikkel, bly, vanadium og zink. Resultaterne af undersøgelserne viser, at der for de fleste metaller findes lidt højere koncentrationer i landets sydlige og østlige egne, mens niveauet generelt er lidt lavere i Midt- og Vestjylland. Ved en sammenligning mellem Danmark, Island og Grønland, ses det, at metaller med typisk antropogen oprindelse (cadmium, bly og zink) findes i betydeligt højere koncentrationer i Danmark, mens metaller, som typisk har oprindelse i jordstøv eller vulkansk aktivitet, ligger på et betydeligt højere koncentrationsniveau i de vegetationsløse arktiske egne. Der fandtes ikke nogen signifikant forskel på koncentrationsniveauet i Danmark og Nordtyskland. Sammenlignet med den tilsvarende undersøgelse i 1980 ses det, at koncentrationen af de stoffer, der hovedsagelig stammer fra forbrænding af olie, er faldet, hvorimod koncentrationer af stoffer, der emitteres ved forbrænding af kul, er steget. Der er et svagt fald i blykoncentrationen, hvilket kan henføres til nedsættelsen af blyindholdet i benzin, selvom trafikintensiteten er steget i perioden.

LECTURES AND POSTERS

1.1 K.Heydorn:"Quality Assurance by the Analysis of Precision".Middle East Technical University. Ankara 30th March 1989.

1.2 K. Heydorn:"Reference Methods for the Determination of Selenium in Biological Materials".Çukurova University, Adana 4th April 1989.

1.3 K. Heydorn:"Factors affecting the levels of vanadium observed in human serum". Nuclear Analytical Methods in the Life Sciences, Gaithersburg 20th April 1989.

1.4 K. Heydorn: "Quality Assessment of Nuclear Methods". National Institute of Standards and Technology, Gaithersburg, 20th April 1989.

1.5 K. Heydorn: "INAA - Application and Limitation". 11th International Symposium on Microchemical Techniques. Wiesbaden 28th August 1989.

1.6 K. Heydorn:" Neutron Transmutation Doping of Silicon: Why and How?". Instituto de Pesquisas Energéticas e Nucleares. Sao Paulo, 14th Sept. 1989.

1.7 K. Heydorn: "Neutronaktiveringsanalyse som referencemetode". Konference om Sporelementer, Hindsgavl, Oct. 1989.

1.8 K. Heydorn: "Advance prediction of single- and double-escape peak areas in gamma-ray spectrometry". American Nuclear Society Winter Meeting, San Francisco, Nov. 1989.

1.9 Henrik Kalfod Nielsen: "Hurtig beta- og gamma-strålings spektrometri". Danmarks Tekniske Højskole, Lyngby, Nov, 1989.

2.0 K. Heydorn; "Neutron Activation Analysis". Course on Metal Toxicology, Landskrona, Dec. 1989.

2.1 P. Solgaard:"Multielement isotopfortyndingsanalyse med ICP/MS". Lis Vinther Kristensen, Per Solgaard. Poster på Sporelementer,Hindsgavl Oct. 1989.

2.2 P. Solgaard: "ICP/MS . Nye perspektiver i uorganisk analyse". Sporelementer, Hindsgavl Oct. 1989.

2.3 Helge Egsgaard,Erik Steen Jensen and Elfinn Larsen:"Nitrogen Isotope Measurements". The 7th Nordic Conference on Mass Spectrometry. January 1989 Geilo, Norge.

2.4 Carsten Theisen Pedersen, Niels Haunsø, Elfinn Larsen, Jan Rud Andersen and Helle Holmsberg:"Sulfamethazine, Measured by GC-MS and LC-MS". The 7th Nordic Conference on Mass Spectrometry,January1989, Geilo, Norge.

2.5 Helle Holmsberg, Jan Rud Andersen, Elfinn Larsen, Carsten Theisen Pedersen, Henning Knudsen and Christian Friis:"A

Comparison of TLC, GC-MS, HPLC and ELISA-Methods for Sulfamethazine Determination in Pork". 35th International Congress of Meat Science and Technology. August 1989. Copenhagen.

2.6 Helge Egsgaard and Lars Carlsen: "Intermediary species studied by mass spectrometry". 7th Nordic Conf. Mass. Spectr., Geilo, January 1989.

2.7 Lars Réne Lindvold and Helge Egsgaard: "A preliminary investigation of dye-sentised gelatin as a volume phase recording material for holographic optical elements". The 2nd Int. Conf. on Holographic Systems, Components and Applications. Bath,UK, Sept. 1989.

2.8 A.B. Hansen:" Experimental Characterization of Petroleum Fractions". Nordisk Ministerråd Seminar on Oil Technology, Fredensborg, Denmark, April 1989.

2.9 A.B. Hansen and E. Thomsen,DGU:"Biomarkers,molecular indicators of source input, depositional environment and source rock maturity. Examples from the Dansih Central Trough". Basin Workshop II, Aarhus Univ., April 1989.

3.1 Torben Nielsen:"Analyse af PAH og PAH i atmosfæren". Risø's AUC Luftforureningsseminar. Nov. 1989.

3.2 Torben Nielsen: "OCOVA-DANI-CET" og dannelse og forekomst af PHN og nitro-PAH i atomsfæren". RIMI seminar. Forskningscenter Risø, Oct 1989.

3.3 K.H. Jørgensen,H. Christiansen, G.A. Mackenzie and K. Brodersen: "Application of the ECCES Model to Forest Soils". Risø National Laboratory, Denmark, May 1989.

4.1 K. Almdal and W. Batsberg Pedersen: "Begrænsninger ved absolut (LALLS/RI) og konventionel kalibrering af SEC kolonner". Nordiske polymerdage 1989, H.C. Ørsted Institutet, Copenhagen, June 1989.

4.2 K. Almdal: "Karakterisering af polymerer ved dynamisk Lysspredning", Defence of Ph. D. thesis, University of Copenhagen, June 1989.

4.3 R.H. Berg, K. Almdal, W. Batsberg Pedersen, A. Holm, J.P. Tam and R.B. Merrifield: " A Simple Approach to Rapid Parallel Synthesis of Multiple Peptide Analogs", 11th American Peptide Symposium, La Jolla, California, U.S.A.,July 1989.

4.4 R.H. Berg, K. Almdal, W. Batsberg Pedersen, A.Holm,J.P. Tam, and R.B. Merrifield: "Polystyrene-Grafted Polyethylene: Design of Film and Felt Matrices for Solid-Phase Peptide Synthesis", 1st Int. Symp. on Innovation and Perspectives in Solid-Phase Synthesis, Oxford,U.K. Aug.-Sept. 1989.

4.5 K. Heller: "Præperativ fraktionering af pektin og bestemmelse af molmasse fordeling vha. SEC/LALLS/RI", Nordiske Polymerdage 1989, H.C. Ørsted Institutet, Copenhagen, May-June 1989.

4.6 S. Hvilsted: "Opening of Nordiske Polymerdage 1989". H.C. Ørsted Institutet, Copenhagen, May-June 1989.

4.7 S. Hvilsted: "Determination of Structural Units in Saturated Multicomponent Polyesters by ^{13}C NMR Spectroscopy". Dip. di Science e Technologie Chimiche, Tor Vergata University, Roma, Oct. 1989.

4.8 W. Batsberg Pedersen: "Størrelses exclusionschromatografi og præparative anvendelser af chromatografi", Analytikerringen, Royal Danish School of Pharmacy, lectures, 12th Jan. and 24th Aug. 1989.

4.9 W. Batsberg Pedersen: "Modification of polymers by irradiation", 7th Int. Meeting on Radiation Processing, Noordwijkerhout, Holland, April 1989.

4.10 W. Batsberg Pedersen: "Irradiation of Polymers". Surgical uses of Polymers, COMETT-Meeting, Copenhagen, June 1989.

5.1 Ole John Nielsen:"Atmospheric Chemistry of Methylchloroform". Odense (DK), June 1989.

5.2 Ole John Nielsen et al., "Atomspheric Degradation of Methylchloroform". Gas Kinetics Discussion Group. York (UK) July 1989.

5.3 Ole John Nielsen: "Gas phase kinetic studies at Risø National Laboratories". Univesity of California Berkeley, July 1989.

5.4 Ole John Nielsen, Howard Sidebottom, Oliver Rattigan, and Jack Treacy: "Atmospheric removal processes for 1,1,1-trichloroethane". 2nd International conference on chemical kinetics, Washington DC, July 1989.

5.5 Ole John Nielsen, Michael Donlon, Howard Sidebottom, and Jack Treacy: "Reactions of OH radicals with alkyl intrates". 5th European Symposium on Physico-Chemical Behavior of Atmospheric Pollutants, Varese, September 1989.

5.6 Ole John Nielsen, Howard Sidebottom, Oliver Rattigan, and Jack Treacy: "Atomospheric removal processes for chlorine containing compounds". 5th European Symposium on Physico-Chemical Behavior of Atmospheric Pollutants, Varese, Sept. 1989.

5.7 Ole John Nielsen, Thomas Ellermar, Jette Munk and Palle Pagsberg:" UV spectrum and kinetics of the trichloromethyl radical". 5th European Symposium on Physico-Chemical Behaviour of Atmospheric Pollutants, Varese, Sept. 1989.

5.8 F. Negri, G. Orlandi, A.M. Brouwer, F.W. Langkilde and R. Wilbrandt, "Force field calculations for the transient resonance Raman spectra of hexatriene in their T_1 state".Third European Conference on the Spectroscopy of Biological Molecules, University of Bologna, Rimini, Italy, Sept. 1989.

5.9 R. Wilbrandt, F.W. Langkilde,F. Negri,G. Orlandi, A.M. Brouwer, "Time-resolved resonance Raman spectroscopy". European Conference on Mole-

cular Spectroscopy, Dresden DDR Sept. 1989.

5.10 Bobrowski, K., Holcman, J., Wierzchowski, K.L., "Intramolecular charge transfer in model peptides and lysozyme involving tryptophan and tyresine". Biophysical Society, 33th Annual Meeting, Cincinnati, Ohio,USA, Febr. 1989.

5.11 Bobrowski, K.,Holcman, J., Wierzchowski, K.L.,"Temperature dependence of intramolecular electron transfer as a probe for predenaturational changes in lysozyme". 8th Conference of Polish Radiation Research Society,Poznan,Poland,March, 1989.

5.12 Bobrowski,K., Holcman, J.,"Influence of geometry of the peptide molecule on the stabilization and decay processes in simple model peptides containing methionine". 8th Conference of Polish Radiation Research Society, Poznan,Poland March 1989.

5.13 Bobrowski, K., Schöneich, Ch., Holcman,J., Asmus, K-D., "OH radical induced decarboxylation of methionine containing peptides: Influence of charge, protonation state and neighbouring amino acid". The Miller Conference,Windemere Hydro, Wales, UK, April 1989.

5.14 Bobrowski, K., Holcman, J., Wierzchowski,K.L., Ciurak, M., "Sulphur intermediates in chemistry and biology". Summer School NATA-ASI, Maratea, Italy, June 1989.

5.15 Gerstenberg, H.M., Coyne, J.J., Hansen, J.W. , Zoetellef, J., "Calculation of the relavtive effectiveness of alanine for neutrons with energies up to 20 MeV". 10th Symposium on Microdosimetry, Rome, Italy, May 1989.

5.16 Hansen, J.W., "Decay of radiation induced response in alanine following heavy ion exposures". Institute of Oncologyg, Krakow, Poland,Sept. 1989.

5.17 Hansen, J.W. "Calculation of dose-response of alanine exposed to neutrons with energies up to 17 MeV". Institute of Nuclear Physics, Krakow, Poland, Sept. 1989.

5.18 Hickel, B., Dagard, P., Metge, M. ,Sehested, K., "Radiation chemistry of aqueous ammonia". The Miller Conference, Windemere Hydro, Wales, United Kingdom, April 1989.

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